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THE JOURNAL
OF THE
American Chemical Society

VOL. XXVII.—NO. 7.

JULY, 1905.

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Entered at the Post-office, Easton, Pa., as Second-class Matter.

Everything intended for insertion in the Journal should be addressed to the Editor, William A. Noyes, Bureau of Standards, Washington, D. C.

Changes of address should be sent to the Secretary, William A. Noyes.

The dues for 1905 ($5.00) should be sent to the Treasurer, Dr. Albert P. Hallock, 440 First Ave., New York City. Remittances may be by money order or by check on a bank in any of the principal cities of the United States.

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Vol. XXVII. [JULY, 1905.] No 7.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

ON AMORPHOUS SULPHUR: II. ON TWO LIQUID STATES OF AGGREGATION OF SULPHUR, S_λ AND S_μ, AND THEIR TRANSITION POINT.[1]

BY ALEXANDER SMITH, WILLIS B. HOLMES AND ELLIOT S. HALL.

Received May 10, 1905.

When common sulphur is raised to a high temperature and then allowed to cool slowly, the whole of the product is crystalline and completely soluble in carbon disulphide. If the specimen of heated sulphur is chilled suddenly, however, it is a familiar fact that a larger or smaller proportion of the material, after it has hardened, is amorphous and insoluble. In a preliminary paper[2] the authors have shown that when carbon dioxide, or better still ammonia, is led for a few minutes through the molten sulphur no insoluble sulphur is found after chilling. The resulting crystalline sulphur, if used at once, may be heated to the boiling-point, or any lower temperature, and chilled without the production of any amorphous sulphur. Sulphur dioxide, however, restores the

[1] Presented in abstract at the Philadelphia Meeting (Dec., 1904) of the American Chemical Society. The first paper of this series, "On Amorphous Sulphur: I. The Relation of Amorphous Sulphur to the Freezing-point of Liquid Sulphur," appeared in the Decennial Publications of the University of Chicago, Vol. IX, p. 55. It was published also in *Z. physik. Chem.*, **42**, 469 (1903).

[2] *Ber.*, **35**, 2992 (1902). In a paper following the present one, No. III, a more complete series of experiments on supercooling will be communicated and in it the relation of the insoluble sulphur to the phenomena described in the present paper is determined

capacity to give insoluble sulphur. When the treatments are used alternately, the result is determined by the last of the two gases which has been employed. Sulphur used immediately after recrystallization also yields no insoluble sulphur. In the course of the further investigation of this phenomenon the question arose: Whether the ammonia, for example, actually destroyed and removed the insoluble sulphur which was in solution in the liquid soluble sulphur, or whether it simply altered the behavior of the former so that it reverted to soluble sulphur more rapidly and thus disappeared during even the most rapid chilling. The present investigation was originally undertaken as one means of securing light on this point. The bearing of the subject of this paper upon the point in question was briefly as follows: It had been shown in the first paper of this series[1] that the freezing-point of soluble sulphur is depressed by insoluble sulphur in accordance with Raoult's law. It was therefore to be expected that this substance would also displace another transition point, of which there was reason to suspect the existence in melted sulphur in the neighborhood of 160-170°. If therefore this transition point should be found to exist, and if two kinds of specimens, which when chilled respectively did and did not yield insoluble sulphur, should be found to give *different* values for the temperature of the transition, the actual destructon of the dissolved insoluble sulphur might reasonably be inferred. If, on the contrary, all specimens showed the *same* transition point, then the same proportion of insoluble sulphur was present in both kinds at that temperature and the seeming destruction was due to rapid reversion during the supercooling. The results, which are described below, showed that a sharp transition point did exist, and that in all specimens it occurred at precisely the same temperature.

I. THE PRESUMED TRANSITION POINT.

Introductory.—It is well known that sulphur melts at about 115°, giving a pale yellow, mobile liquid and that between 160° and 170° it becomes deep brown in color and suffers a rather sudden access of extreme viscosity. Berthelot[2] supercooled sulphur at various temperatures and estimated the amount of insoluble sulphur. He found that almost none of this form was obtainable below 170° while 25-30 per cent. was always secured

[1] *Proc. Roy. Soc.* (Edin.), **24**, 299 (1902); *Z. phys. Chem.*, **42**, 469 (1903).
[2] *Ann. ch. ph.* (3), **49**, 476 (1857).

from specimens which had reached higher temperatures. Special means of chilling enabled him to increase the yield. He inferred therefore that at 171° the whole of the sulphur was transformed into insoluble sulphur and that the sudden thickening of the liquid coincided with this change. More exact measurements,[1] made by the same procedure, showed us that there were considerable and continuously increasing quantities of insoluble sulphur in sulphur even below 170° and demonstrated that Berthelot's method of experiment was not capable of giving results to justify his conclusion. Furthermore, sulphur treated with ammonia, and so bereft of the capacity to yield insoluble sulphur, still became thick at 170°, so that the existence of an intimate connection between the viscosity and the content of insoluble sulphur was also, for a time, in doubt.

Careful measurements of the variation in the viscosity with change in temperature, made by Brunhes and Dussey,[2] indicate that the mobility of the liquid increases from 115° to 156-157° in the ratio 5 : 9. From this point the mobility diminishes very rapidly. At 162° the liquid is extremely viscous and at 180° the minimum of mobility is reached.

Frankenheim[3] seems to have been the first and only observer to offer an explanation of the viscosity. From a study of the irregularities in the rate at which constantly heated sulphur rises in temperature he concludes that there is one, and only one point at which a definite absorpton of heat always occurs. This is at 260°. He infers that a transformation into a new liquid state takes place at this point. He explains the extreme viscosity from 170-260° by the theory that the separation of the new liquid begins at 170° and goes on throughout this whole region of temperature. In such circumstances the mass is an emulsion of minute droplets of two liquids and owes its viscosity to the ascendency of the surface properties over those natural to either liquid in its separate condition.

Considerations based upon the phase rule make it easy to test this hypothesis. One substance cannot exist in three phases (two liquid and one vapor phase) except as a non-variant system at a single temperature and pressure. It is evident therefore that an

[1] The results will be given in another paper.
[2] *Compt. Rend.*, **118**, 1045 (1891).
[3] *J. prakt. Chem.*, **16**, 5 (1839).

extended region of stable coexistence for two liquid forms is impossible. On the other hand, many facts show that a state of unstable equilibrium cannot persist in sulphur at 170-180° for more than a few minutes. To test the above hypothesis we therefore kept a specimen of sulphur at 180° constantly for several days. Since during this time no diminution in the viscosity was perceptible, we inferred that great viscosity is a specific property of sulphur at that temperature.

Several other facts, to be mentioned later, were also known when this work began, and these indicated some temperature below 170° as the probable transition point.

Although the existence of two states of a liquid has not previously been established in any perfectly simple case, yet the sharp transition of "crystalline liquids"[1] to isotropic liquids is to a certain extent parallel to what we expected to find. It is true that the peculiar organic compounds which show such a transition melt first to give "liquid crystals" which are optically active, while liquid sulphur is found to be isotropic at all temperatures, so that in this respect the analogy fails. There is, however, no necessity for believing that some special mode of orientation of, or in, the molecules is a condition essential to the existence of a distinct liquid form. A certain degree of mutual insolubility would be sufficient to cause the separation of a new phase and would lead to the appearance of a transition point. That one form of sulphur—the amorphous form—could exist in solution in another form—the soluble one—and behave in all respects like a foreign solute was shown by the fact that it depressed the freezing-point of the material.[2] Since two liquid states of the same substance are not likely to be completely immiscible, it is to be expected that a certain amount of the liquid form which predominates above the transition point (S_μ) will be formed below this point and will exist in solution in equilibrium with the other liquid (S_λ). The transition will then be determined by the fact that the liquid proper to the lower temperatures has at length become saturated with S_μ. This will then separate, as from a supersaturated solution, and the new phase will then contain some

[1] Shown by cholestryl benzoate (Reinitzer: *Monatshefte*, **9**, 435) and by *p*-azoxyphenetol and *p*-azoxyanisol (Gattermann: *Ber.*, **23**, 1738). For a physico-chemical study of these cases see Schenck: *Z. phys. Chem.*, **23**, 703; **25**, 337; **25**, 349; **27**, 167; **28**, 280; **29**, 546; Hulett: *Ibid.*, **28**, 629.

[2] Smith and Holmes: *Z. phys. Chem.*, **42**, 469.

of the liquid proper to the lower temperatures (S_λ) as a solute in S_μ. The S_λ will then gradually become less in amount as the temperature rises.

The Methods Used.—There are several methods which should be available for ascertaining definitely whether a transition point exists, and for determining its exact location. When such a point occurs there must be a sharp discontinuity at the transition temperature in the rate at which every physical property changes with temperature. Curves representing viscosity, dilatation, solubility, vapor-tension, refractive index, etc., must all take a new direction at this point. We employed the first three of these properties. At such a point, also, as at the melting-point of a solid, an absorption of heat should be observed, and this was found to be the case with sulphur. By these means it was shown that a transition does occur and that it takes place at 160°. We have designated the liquid forms S_λ and S_μ. The former is the predominating substance up to 160° and the latter for an undetermined distance beyond this temperature. With the exception of one set of observations at 220-266°, no attempt has yet been made to explore the region above 160°.

II. CHANGE IN MOBILITY AT THE TRANSITION POINT.

Object of the Experiments.—The measurements of Brunhes and Dussey placed the onset of the viscosity at 156-157°. Their results may be accepted in spite of the fact that our observations place the transition at 160°. It is to be expected that the two liquid forms of sulphur will be somewhat miscible and that therefore the S_μ dissolved in the S_λ will lead to a perceptible increase in the viscosity of the latter below the temperature at which the transition actually takes place. In this connection, therefore, our only task was to ascertain whether or not sulphur treated with ammonia, and incapable of giving insoluble sulphur, shows the same behavior as ordinary sulphur. We had observed previously[1] that such sulphur does become viscous. It remained only to ascertain whether it did so at the same or at a different temperature.

Experimental Method.—Preliminary experiments proved that it was easy, by too rapid heating, to overshoot the minimum temperature at which the viscosity could appear. This was to be expected, since supersaturation of the S_λ with S_μ might readily

[1] *Ber.*, **35**, 2993.

occur and the separation of the new phase be postponed to a higher temperature. A method of raising the temperature very slowly and in an easily controllable fashion was necessary in order that there might be time for a continuous adjustment of the material to the state of equilibrium proper to each temperature. A bath of *o*-dichlorhydrin (b. p. 174°) boiling under reduced pressure was therefore employed for heating. Its temperature was altered by changing, a very little at a time, the pressure under which it boiled[1]. In the neighborhood of the transition point the temperature was not allowed to rise faster than 1° per hour. The apparatus consisted of an outer tube such as is used in V. Meyer's method for measuring vapor-density. This contained the dichlorhydrin. An inner tube contained melted paraffin, the presence of which enabled us to secure a steady rise in the temperature of the sulphur in spite of the slightly discontinuous nature of the changes in the temperature of the vapor-bath. The tube containing the sulphur stood in the paraffin. It was not, as with Brunhes and Dussey, our purpose to observe the point of maximum mobility, but to find a point a little above this at which a noteworthy degree of viscosity had appeared. By means of a fine platinum wire with a loop at the end the first appearance of such viscosity could easily be ascertained within 0.5° or less. At 159° the sulphur appeared, by this means of observation, to be as mobile as at 120°; at 160° it was so thick that the wire sank with difficulty. This degree of accuracy was sufficient for our purpose, since it was here simply a question of whether or not 12 per cent. of a foreign substance was present.[2]

Pure recrystallized rhombic sulphur which had been kept in the laboratory for months was used.

Results.—The temperatures at which viscosity first became perceptible were as follows:

Ordinary sulphur, 159.5°; 159.7°; 159.1°. Mean, 159.4°.

Sulphur treated with ammonia, 159.5°; 159.5°; Mean, 159.5°.

Ordinary sulphur chilled from 160° gives 11 per cent. of insoluble sulphur. To make certain that no error had been committed,

[1] Ramsay and Young: *J. Chem. Soc.*, **47**, 640 (1885). A large vacuum-reservoir and automatic pressure-regulator made possible the maintenance of any required temperature for any length of time.

[2] An experiment described later enabled us to calculate, roughly, that the presence or absence of this amount of a body of molecular weight S_8 (*Z. phys. Chem.*, **42**, 479) should have made a difference of 36° in the transition point.

one of the specimens of sulphur treated with ammonia was chilled and was found to give on extraction no insoluble sulphur whatever.

The experiments in this and the following sections were all repeated with distilled sulphur, because its behavior was always somewhat different from that of crystallized sulphur. It appeared to be much more liable to become superheated. Thus, with it, no viscosity could be observed at 160°, even when the fluid was kept for half an hour at this temperature. The viscosity appeared first at 161.5-162° and even then asserted itself rather gradually. While no cases of superheating a solid are known, the superheating and supercooling of liquids are both familiar. Hence no doubt was felt in regard to the correctness of this explanation.

III. HEAT ABSORPTION AT THE TRANSITION POINT.

Previous Observations.—Marx[1] was the first to observe irregularities in the rates of heating and of cooling in sulphur. Frankenheim[2] found that specimens submitted to different rates of heating, and even different specimens heated in the same way, behaved differently. He attributed all the irregularities, save a noticeable one at 250-260°, to unequal heating or cooling due to changes in viscosity. At 250-260°, with rising temperature, a marked absorption of heat was shown by all specimens. On cooling, a development of heat at this point caused a delay in the fall in temperature. Deville,[3] on the other hand, found the behavior at 250-260° normal; but he believed he had evidence, as the temperature rose, of an evolution of heat at 120-160° and again between 180-230°. In cooling there was a slight evolution of heat at 240-210°, an absorption at 180-160°, possibly a slight evolution at 160-145°, and an absorption at 145-135°. He considered the release of heat between 240° and 210° as the only significant part of the phenomena and related it to the fact that the greatest viscosity existed between these temperatures. Schaum[4] found that sulphur standing in a bath of constantly rising temperature showed a notable absorption of heat, indicated by a sudden drop in temperature, near 168°. Thus on different occasions the thermometer fell from 168.0° to 166.3°, from 168.6°

[1] *Schweigg.*, **60**, 1 (1830).
[2] *J. prakt. Chem.*, **16**, 7 (1839).
[3] *Ann. ch. ph.* (3), **47**, 94 (1846).
[4] *Ann. Chem.* (Liebig), **308**, 25 (1899).

to 166.8° and from 167.8° to 166.8°, before beginning to reascend.

In none of these cases is any mention made of an attempt to avoid unequal heating by the use of stirring apparatus.

The Need of Stirring.—The eccentricities in behavior when stirring is not employed were illustrated strikingly in our first experiments by this method. Thus the readings of the thermometer at intervals of one minute, during part of one experiment, were as follows: On heating: 157.5°; 160°; 162°; 164°; 166°; 167°.5; 166.5°; 168°; 170°; 172°. In cooling: 175.5°; 172°; 168.5°; 164.5°; 159.5°; 145°; 138.5°; 134°; 129.5°. As the temperature rose, the ascent from 164° to 166° took one minute, while that from 167.5° to 168° took two minutes. As the temperature fell the descent at 168.5 was 4° per minute, and at 159.5° it was 14.5°. In other words, heat appeared to be absorbed near 160-170° both in ascending and in descending, a result in conflict with the laws of energy! The cause of the sudden drop in temperature as the thermometer fell was traced to the adhesion of a mass of viscous, poorly conducting sulphur to the bulb of the instrument and its sudden displacement by the mobile and cooler sulphur from the layers which, being nearer to the sides of the tube, had lost heat more rapidly by radiation.

The Tendency to Various Degrees of Superheating.—Even when the sulphur was stirred vigorously, however, the temperatures at which absorption of heat was observed with ascending temperature were different with every experiment. Thus specimens of ordinary melted rhombic sulphur showed it at 169°, 167°, and 170.5° according to the rate of heating. Similar specimens treated with ammonia gave slighter evidence of the absorption and the temperatures were sometimes lower: 160-162°, 167.5°, 161°. Specimens specially recrystallized from other solvents than carbon disulphide gave more marked effects. The solvents used and the points at which the absorption of heat was observed were as follows: Chloroform, 176° (fell to 171.5°); toluene, 183° (fell to 177.8°). Sulphur twice distilled and then recrystallized from carbon disulphide fell from 179° to 174.5°. Distilled sulphur showed either no interruption whatever in the steadiness of the rise in temperature, or at most a very slight one.

In all cases in which any evidence of absorption of heat was noticed, the sulphur became suddenly viscous at the same mo-

ment. With the distilled sulphur the viscosity appeared more gradually.

It was evident that with this method of experiment, in which there was a rapid ascent of the temperature, the various specimens of sulphur suffered superheating in various degrees and the observations were of no value except as evidence of the fact that small traces of impurities had a great effect upon the facility with which superheating occurred.

The Minimum Temperature at which Heat Absorption Could Be Observed.—To avoid overshooting of the transition point caused by the rapid rate at which the temperature rose, a bath was arranged so that its temperature could be maintained at some fixed point. The sulphur contained in a tube was placed in this bath and vigorously stirred. Thermometers in the bath and in the sulphur enabled the temperature of each to be read. It was found that when the sulphur, prepared by melting the crystalline material, was kept for a sufficient length of time at 162.5° or any higher temperature, a sudden fall, accompanied by thickening, ultimately set in. Often half an hour elapsed before the drop in temperature was observed. When the sulphur was held at temperatures lower than 162.5°, no fall in temperature occurred. On only one occasion did the temperature fall so low as 161.5°, in the other cases it fell to 162°. Sulphur recrystallized from toluene showed the effect very sharply, the temperature remaining for fifteen minutes at 163° and then suddenly falling to 162°. Distilled sulphur, however, could not be made to show any evidence of heat absorption at 163° and became viscous gradually at this temperature. Inoculation with brown viscous sulphur had no decided effect in any of the experiments.

Sulphur, prepared by melting crystalline sulphur, behaved after treatment with ammonia, exactly like that which had not been so treated.

The experiments made by this method could not give the exact transition point, but the results showed that the point was certainly below 162°. They demonstrated also that for different specimens of sulphur the position of the point was the same, whether the specimens were such as, when chilled, give insoluble sulphur or not.

IV. THE SOLUBILITIES OF THE TWO LIQUID FORMS OF SULPHUR.

Preliminary Experiments.—It was expected that the two

liquid forms of sulphur would show different curves of solubility in the same solvent. The very first experiments gave even more striking evidence of this than had been hoped. Sulphur was found to dissolve freely in melted diphenylmethane, diphenyl, β-naphthol, and triphenylmethane, and that with little or no evidence of chemical interaction even at 200°. In these substances sulphur seemed to be very soluble at about 170°. In each case, when the solution was allowed to cool to the saturation point, liquid sulphur separated. In each case, when the temperature was once more raised, the emulsion first became clear and then at a much higher temperature (above 170°) liquid sulphur began to separate once more. Thus with 18 grams of sulphur and 10 grams of triphenylmethane the separations occurred at 147° and at 214.5°.

Since the *same* substance cannot be in equilibrium with solutions of the same concentration at two different temperatures it follows that either the dissolved sulphur underwent a change, or the sulphurs which were deposited and remained in contact with the solution were different. In each case, the sulphur which separated on cooling was pale yellow and mobile, while that which separated on heating was deep brown and viscous. It appeared therefore that it was the sulphur phase which was different. In view of van't Hoff's law, it was further evident that S_λ dissolved in these solvents with absorption of heat and should show an ascending curve of solubility, and that S_μ dissolved with evolution of heat and should show a descending curve of solubility.

The sulphur phase which appeared was, of course, in each case a solution of the solvent in sulphur and not pure sulphur. A sudden clouding of the sulphur phase itself, which occurred when it was allowed to cool, was due to the formation of a new phase consisting mainly of the original solvent.

We were unable to find any solvent for which the solubility could be measured throughout the whole range from 110° to 210°, without the occurrence of complete miscibility near to 160-170°. The intersection of the two curves, therefore, could not be observed. Hence these experiments demonstrate only the absolutely different nature of the two liquids and do not lead to a measurement of the transition point. This is a matter of small moment however, because the point of intersection, if found, would be the one at which the solution is in equilibrium with two solutions of

the solvent in sulphur, and not with two pure forms of sulphur. The temperature of the intersection might, therefore, be far removed from the transition point.

The Method and Results of Solubility Measurements.—For measuring the solubilities the synthetic method was used. A weighed quantity of the organic solvent was taken and to it was added a weighed quantity of sulphur. The mixture having been heated by means of a bath of melted paraffin until it was clear and homogeneous, the flame was removed and the temperature at which clouding began was taken. After verification of this point, an additional known quantity of sulphur was thrown in and the process repeated. The points of saturation at the higher temperatures were obtained in corresponding fashion. Pure recrystallized sulphur was used. The results were as follows:

Triphenylmethane.—The saturation points for S_λ, at lower temperatures, are on the left, those for S_μ on the right. The first column (S) gives, in each case, the proportion of sulphur to 10 grams of triphenylmethane; the second column (t), the temperatures of clouding.

S_λ.		S_μ.	
S.	t.	S.	t.
4.47	108.5	18.20	214.5
5.48	117.0	20.74	211.0
7.02	127.0	25.15	206.0
8.09	131.0	30.89	203.0
9.68	136.5	36.29	200.0
11.46	141.0	42.19	199.0
13.37	144.0	54.85	198.0
16.45	146.0		
19.68	146.5		
23.04	147.0		
29.33	146.0		

The curves are shown in Fig. 1, in which the temperatures are laid off horizontally and the concentrations vertically. The last observation (146°) on the lower curve is on the upper branch of this curve and in this experiment, as is to be expected, it was triphenylmethane which separated and not sulphur.

β-Naphthol.—With this substance two series of measurements of the lower saturation points were made. In the first (I) ordinary crystallized sulphur was used, in the other (II) sulphur which had been treated with ammonia[1]. No observations of the

[1] In the latter case, however, when the solution was suddenly chilled from 163°, after the measurements had been completed, 4.3 per cent. of insoluble sulphur was found in the product (see next paper, section. 7).

higher saturation points (above 200°) were made, as there was some chemical interaction.

I.		II.	
S.	t.	S.	t.
3.40	118.0	4.88	134.5
4.66	132.5	9.74	157.0
5.93	143.5	11.93	160.5
7.00	149.5	14.51	162.5
8.41	154.0	17.76	163.5
(Tube broken and series interrupted.)		20.97	164.0
		23.81	163.8
		26.48	163.8
		30.00	163.0

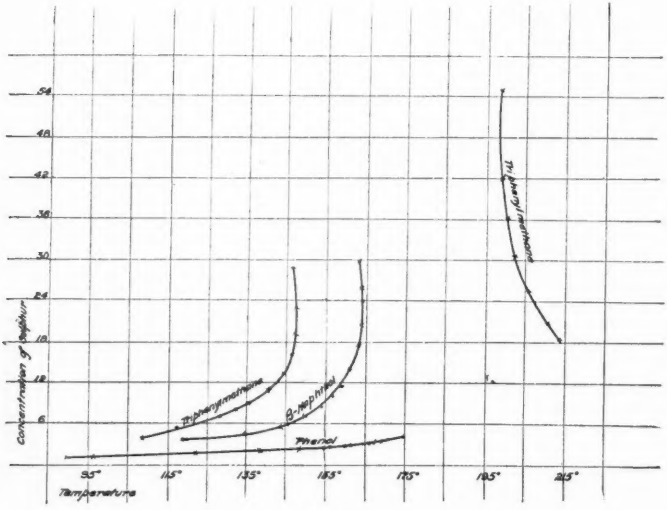

Fig. 1.

The last two observations of the second set showed separation of β-naphthol, and lie upon the upper branch of the curve (Fig. 1).

Phenol.—The series with phenol was naturally limited to the region below the boiling-point (183°) of the organic compound. Sulphur which had been melted and treated with ammonia was used.[1]

[1] When the homogeneous solution, containing 27 per cent. of dissolved sulphur, was suddenly chilled from above 175°, 4.84 per cent. of insoluble sulphur was found in the residue.

S.	*t.*	S.	*t.*
0.91	89.5	2.96	162.0
1.04	96.5	3.07	164.5
1.53	122.5	3.16	166.0
1.99	138.0	3.24	167.5
2.36	148.5	3.35	170.0
2.63	155.0	3.49	172.0
2.71	157.5	3.65	175.0
2.86	160.5		

The curve derived from these results (Fig. 1) shows no break although the maximum temperature is considerably above the transition point. The experiments to be described in the next section, however, show that the transition point is greatly raised by the presence of a dissolved body in the sulphur, so that the transition point of sulphur saturated with phenol may be considerably above even the highest temperature (175°) here attained.

In the effort to secure continuous measurements extending past the transition point, several series of observations were made, using solutions of sulphur in triphenylmethane with which various proportions of phenol had been mixed. It was hoped thus to reduce the solubility values, which, with triphenylmethane, are extremely high. In these experiments a point as high as 180.5° was reached without any break in the curve being encountered. Only one observation from these sets will be given. It was one in which the double separation of sulphur appeared. With 2.5 grams phenol, 7.5 grams triphenylmethane and 25.36 grams sulphur, separation of sulphur occurred at 158.5° and again at 208.5°.

V. DILATOMETRIC STUDY OF THE TRANSITION POINT.

Previous Measurements.—The only complete series of measurements of the coefficient of expansion of sulphur from 110° to the boiling-point was made by Moitessier[1]. The values he found were as follows:

110–120°	0.000551	225–250°	0.000338
120–140°	0.000490	250–275°	0.000358
140–160°	0.000380	275–300°	0.000374
160–180°	0.000210	300–350°	0.000401
180–200°	0.000262	350–400°	0.000437
200–225°	0.000320	400–440°	0.000469

These figures show a very sharp descent to 160-180° and a rapid ascent beyond it. When they are plotted, the curve is V-shaped

[1] *Mem. Acad. de Montpellier*, **6**, 107 (1864).

with the minimum exactly at 170°. Moitessier attributed the diminution in the coefficient to the formation of increasing amounts of insoluble sulphur. Presuming that this body in liquid form was much denser than soluble sulphur, his theory was that its production caused a shrinkage which reduced the natural expansion of the sulphur. He made a series of measurements of the amounts of insoluble sulphur obtained by chilling sulphur which had been kept at various temperatures and found that the amount rose steadily to 22.6 per cent. at 179.4°. At 213.5° it was 27 per cent. and at higher temperatures about the same. Thus he thought that either the proportion of insoluble sulphur became constant above 180°, or possibly the whole of the sulphur had been transformed into this modification. In either case the coefficients beyond that temperature were those of a substance whose composition no longer changed.

Moitessier observed that a certain length of time was required before the sulphur reached a state of equilibrium at each temperature. Thus when a charged dilatometer was suddenly moved from a bath in which it had been kept at 140° to one of which the temperature was 171° the following were some of the readings which were obtained at intervals of a minute:

Time.	1′.	2′.	3′.	4′.	5′.	6′.	7′.	8′.	15′.
Reading.....	47.5	48.2	48.5	49.0	48.5	47.9	47.8	47.8	47.8

Apparently the sulphur reached the new temperature in four minutes and showed at that time its maximum volume. Three minutes more were needed, however, for the accomplishment of an internal change, and the constant volume was reached at the end of seven minutes from the start. It will be noted that in this experiment the material had to undergo the transition which we have found to occur at 160°. A similar experiment in which the dilatometer was brought rapidly from 135° to 163° showed a much smaller effect:

Time.	1′.	5′.	7′.	15′.
Reading.....	45.0	47.5	47.0	47.0

The Method Used for the Dilatometric Determination of the Transition Point.—When an experiment corresponding to the above is made with solid sulphur in the neighborhood of 95.6°, the dilatometer being filled up with oil, the new temperature is reached in a few minutes, but the change in volume continues for

many hours. The transformation of rhombic into monoclinic sulphur, or *vice versa*, which then occurs is a very slow process. It was easy therefore for Reicher[1] to find two temperatures, one degree apart, at the lower of which monoclinic sulphur changed into rhombic with steady contraction while at the higher the opposite change went on with expansion. At a temperature midway between these points no change in volume was observed. In the present instance the transition in the melted sulphur is accomplished almost as soon as the new temperature is reached, and hence the volume-changes accompanying the two phenomena are superposed and difficult to distinguish. Reicher's method is thus inapplicable to the transition from S_λ to S_μ. We therefore decided to determine the location of the transition point more exactly by measuring the dilatations in the neighborhood of the point at shorter intervals than those used by Moitessier.

The form of the apparatus, and the method of maintaining a succession of constant temperatures were the same as those employed in the observations of the onset of viscosity. The bulbs of the dilatometers held about 20 cc. and a length of the attached capillary tube equal to one division on the arbitrary scale employed contained approximately 0.0004 cc. The dilatometer, after being filled, was kept at the first temperature for one to one and a half hours to permit complete adjustment of the sulphur to a condition of equilibrium. At each succeeding temperature the final reading was not recorded until a number of tentative observations had shown that the volume had become constant. In this way the sulphur remained from twenty-five to forty minutes at each temperature. Near to the transition point readings were made at intervals of 1°.

The materials used were: (1) sulphur twice distilled; (2) sulphur twice distilled, then melted and treated with ammonia; (3) recrystallized sulphur, melted and treated with ammonia. There were two sets of observations in each of these three cases. The first, with an ascending series of temperatures, involved the transition from S_λ to S_μ. The second, made immediately afterwards with the same filling of the dilatometer, involved the opposite transition with a descending series of temperatures.

The dilatometer used in the first and the last of the three sets was calibrated in order that the actual coefficients of expansion

[1] *Zeit. für Krystallographie*, **8**, 593 (1884).

might be ascertained. For the mere purpose of locating the transition point, however, calibration and allowance for the coefficient of expansion of the glass were unnecessary. In the following table, therefore, the uncorrected readings have been used. In the columns headed "Mean temperature" the mean of the temperatures corresponding to two successive readings are given. In the other columns, headed "Expansion for 1°," is given the expansion per degree between two successive temperatures, expressed in terms of the divisions of the arbitrary scale. Thus in the first column 161.3° is the mean of the successive temperatures 160.8° and 161.9°. The expansion on the scale for this difference of 1.1° was 4.7 divisions, or 4.3 per degree.

Distilled S. Ascending series.		Distilled S + NH_3. Ascending series.		Crystallized S + NH_3. Ascending series.	
Mean Temp.	Expansion for 1°.	Mean Temp.	Expansion for 1°.	Mean Temp.	Expansion for 1°.
154.2	17.3	156.6	13.9	154.4	17.5
156.2	13.7	158.4	6.8	157.8	10.8
157.9	8.9	159.9	3.0	160.2	2.6
159.2	6.3	161.1	3.2	161.3	2.9
160.2	4.6	162.2	3.6	162.6	4.2
161.3	4.3	163.5	4.4	164.1	4.4
162.4	4.8	165.0	5.0	166.1	5.4
163.7	5.0			168.3	6.8
166.0	5.6				
168.9	7.0				
Descending series.		Descending series.		Descending series.	
169.9	7.8	167.3	5.8	168.9	7.1
167.7	6.3	165.3	5.4	166.9	6.5
164.6	5.3	162.8	3.6	164.7	6.1
162.4	4.3	160.1	2.8	163.0	4.9
160.8	4.3	157.6	9.8	161.4	4.3
159.8	4.5			160.3	5.0
157.9	9.0			158.7	7.7
154.9	16.9			156.9	13.3
				155.2	16.0

By graphic interpolation, using each of the six sets of observations separately, the following values for the transition point were found:

	Ascending.	Descending.
Distilled sulphur.....	160.2	160.2
Distilled sulphur + ammonia.....	160.0	160.2
Crystallized sulphur + ammonia..	160.2	160.0

The mean of all the results is 160°. It will be seen that there is no difference between the behavior of the samples which, by

treatment with ammonia, had lost the capacity by chilling to give insoluble sulphur, and those which had not. In each case a part of the same specimen was chilled in order to make sure that the treatment had been effective.

The Actual Value of the Coefficients of Expansion of Sulphur near to the Transition Point.—The dilatometer used in the first two of the above three series of measurements had been calibrated, so that the actual values of the coefficients of expansion in this interesting region could be learned.

The capillary tube was fairly uniform in bore and no corrections were made for the very slight irregularities. The bulb and capillary were in all cases completely immersed in the bath, so that no correction was required on this account. The constants of the dilatometer were as follows:

	cc.
Volume of dilatometer at 0° up to zero of arbitrary scale.....	19.738
Volume of capillary per centimeter at 21°.....	0.00616
Volume of capillary per scale division at 21°.....	0.000414

100 scale divisions = 6.72 cm.

Coefficient of expansion of the glass = 0.000029

By calculation, the volume of 1 scale division at 160°, allowing for the expansion of glass, is 0.000415 cc. By calculation, the volume of the bulb to the zero of the scale, allowing for the expansion of the glass, in cubic centimeters and in scale divisions, is: 150°, 19.824 cc. = 47768 scale divisions; 160°, 19.830 cc. = 47782 scale divisions; 170°, 19.836 cc. = 47796 scale divisions. Volumes at intermediate temperatures were obtained from above by interpolation.

In the following tables the second and third columns give the temperature and scale readings. The thermometer employed was compared with a standard thermometer at 100° and agreed with it within 0.1°. The fourth column gives the difference between successive scale readings divided by the difference between the corresponding successive temperatures; this is the apparent expansion per degree. The first column shows the mean of two successive temperatures and the fifth column the corresponding coefficient of expansion. The first series was made with distilled sulphur, and the second with melted crystallized sulphur which had been treated with ammonia. In each of the two series the first set of readings was made with rising and the second with descending temperature.

COEFFICIENT OF EXPANSION. FIRST SERIES. DISTILLED S.

Mean temp.	Temp. reading.	Scale reading.	Apparent expansion for 1°.	Coefficient.
	153.2°	0.0		
154.2°	155.2°	34.7	17.3	0.000363
156.2°	157.2°	62.2	13.7	0.000287
157.9°	158.7°	76.0	8.9	0.000192
159.2°	159.6°	81.4	6.3	0.000125
160.2°	160.8°	87.0	4.6	0.000097⊕
161.3°	161.9°	91.7	4.3	0.000089⊕
162.4°	163.0°	97.0	4.8	0.000102
163.7°	164.5°	104.5	5.0	0.000104
166.0°	167.5°	121.2	5.6	0.000116
168.9°	170.4°	141.5	7.0	0.000146
	170.5°	142.8		
169.9°	169.4°	134.2	7.8	0.000163
167.7°	166.0°	112.6	6.3	0.000132
164.6°	163.3°	98.2	5.3	0.000111
162.4°	161.5°	90.5	4.3	0.000089
160.8°	160.2°	84.9	4.3	0.000090⊕
159.8°	159.4°	81.3	4.5	0.000094
157.9°	156.4°	53.2	9.0	0.000195⊕
154.9°	153.5°	4.2	16.9	0.000338

COEFFICIENT OF EXPANSION. SECOND SERIES. CRYST. $S+NH_3$.

Mean temp.	Temp. reading.	Scale reading.	Apparent expansion for 1°.	Coefficient.
	152.8°	15.3		
154.4°	156.0°	71.4	17.5	0.000367
157.8°	159.7°	111.3	10.8	0.000225
160.2°	160.8°	114.2	2.6	0.000055⊕
161.3°	161.9°	117.4	2.9	0.000060⊕
162.6°	163.3°	123.3	4.2	0.000088
164.1°	165.0°	130.8	4.4	0.000092
166.1°	167.2°	142.7	5.4	0.000112
168.3°	169.4°	157.6	6.8	0.000141
	169.5°	130.5		
168.9°	168.4°	122.7	7.1	0.000048
166.9°	165.5°	103.7	6.5	0.000136
164.7°	164.0°	94.5	6.1	0.000128
163.0°	162.0°	84.7	4.9	0.000102
161.4°	160.8°	79.5	4.3	0.000090⊕
160.3°	159.8°	74.5	5.0	0.000104⊕
158.7°	157.7°	58.2	7.7	0.000162
156.9°	156.2°	38.2	13.3	0.000279
155.2°	154.3°	7.8	16.0	0.000335

In order to secure mean values for the coefficient, all the results were laid down graphically (temperature horizontally and coefficient vertically) in Fig. 2 and a smooth curve was drawn through them. The only points to be regarded as thoroughly trustworthy were those derived from temperature readings, both of which were certainly upon the same branch of the curve. When the readings are on opposite sides of the minimum the point based on them does not show the true direction of the curve. The points about which there can be no question are marked thus: +. The others, indicated by the sign ⊕ upon the diagram and in the tables, are

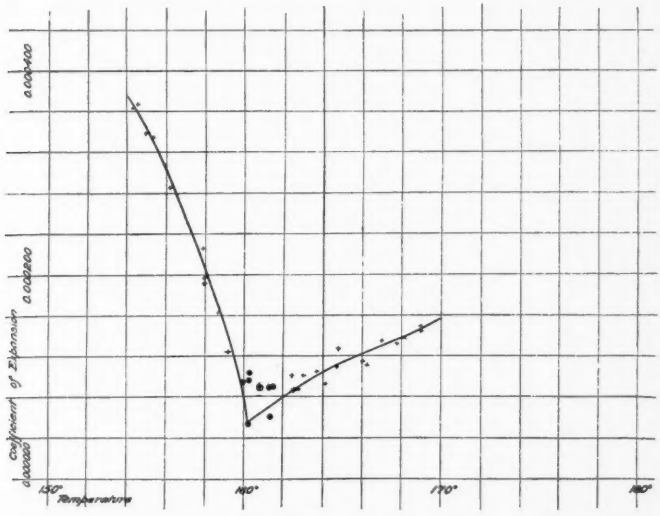

Fig. 2.

based upon readings, one of which was within the region of uncertainty, 159.8-161°. A little consideration will show, however, that of these values the ones corresponding to the lowest coefficients must be the most accurate. In making the curve the two lowest points of this kind have therefore been given the most weight. The following table gives the values of the coefficients of each degree between 154° and 170°, as they may be read from the curve. The mean error outside of the region 1° on each side of the minimum, calculated by taking the average of the vertical distances of the points from the curve, excluding, however, the points marked, ⊕ is ±0.000007.

MEAN COEFFICIENTS OF EXPANSION.

Temp.	Coefficient.	Temp.	Coefficient.
154	0.000376	162	0.000084
155	0.000340	163	0.000096
156	0.000300	164	0.000106
157	0.000252	165	0.000114
158	0.000204	166	0.000124
159	0.000148	167	0.000130
160	0.000076	168	0.000140
160.2	0.000058(min.)	169	0.000148
161	0.000068	170	0.000158

The values for intervals of 20°, such as Moitessier gives, are shown by the above results to be very rough averages for regions in some parts of which the coefficient is six times as great as in others. Thus, for 140-160° he gives the value 0.000380 and for 160-180°, 0.000210. The change in the coefficient is much more extensive and sudden than his results would lead one to expect.

The Transition Point Elevated by a Dissolved Substance.—As has been said, one of our objects was to ascertain whether samples of sulphur, which on being chilled gave insoluble sulphur, showed the same transition point as those which did not. The identity in the values of the transition point found by use of each kind was to be used as a proof that no substance was present at the transition point in the former set of samples that was not present in the latter. To make this inference valid, however, it was necessary to show that a foreign substance purposely introduced did displace the transition point.

Preliminary experiments, made in connection with the observations of the onset of viscosity (Section 2) and of the heat absorption (Section 3), showed that there was such a displacement. Thus with 2 per cent. of phenol the first appearance of viscosity was noticed about 7° above the usual point. Exact measurements, however, could not be made by either of these methods. Further, evidence that there is an elevation in the transition point when phenol is dissolved in sulphur was obtained in connection with the measurement of the solubility of sulphur in phenol, and has been referred to in that connection.

Since the dilatometric method gave the most exact determinations of the transition point, two sets of experiments were made by that method. In these phenol, on account of its well-known tendency to association, was not employed. Two solutions of

triphenylmethane in melted sulphur containing respectively 1 and 2 per cent. of the organic substance were used. The observations were carried out in the same way as those described above, and the data are expressed in the same fashion as before:

Dist'd S + 1 per cent. $CH(C_6H_5)_3$. Ascending series.

Mean temp.	Expansion for 1°.
149.8	11.7
153.5	11.7
157.1	10.2
159.5	7.5
162.5	3.2
164.5	2.9
166.5	3.4
168.5	3.7
170.7	4.4
173.0	4.8
Descending series.	
172.4	5.0
169.4	4.1
166.7	3.4
(163.2	3.6)
159.4	7.4
157.0	10.2
Extra readings	
164.2	2.9
161.7	4.2

Dist'd S + 2 per cent. $CH(C_6H_5)_3$. Ascending series.

Mean temp.	Expansion for 1°.
159.2	11.4
161.4	9.8
164.0	6.1
166.5	4.5
167.5	5.0
169.4	5.0
172.2	5.3
175.4	5.7
Descending series.	
179.5	5.9
176.1	5.4
172.2	5.4

The numbers enclosed in parenthesis were derived from two successive readings at 165.5° and 160.9°. These temperatures were too far apart and lay on opposite sides of the new transition point. Since, therefore, they belonged respectively to the left and right arms of the curve, the numbers derived from them in the usual way did not represent the true direction of the curve at 163.2°. Two extra readings, avoiding these sources of error, were therefore made and were employed in constructing the curve.

The transition points, found by graphic interpolation, were as follows:

Sulphur + 1 per cent. triphenylmethane..... 163.0°
Sulphur + 2 per cent. triphenylmethane..... 165.6°

The value for sulphur alone being 160°, the elevations of 3° and 5.5° respectively are approximately proportional to the amounts of the dissolved substance. The molar elevations, for one mole

of triphenylmethane in 100 grams of sulphur, calculated from these data are 700 and 660, the mean of the values being 680.

Dilatation at 220-266°.—As we have seen, Frankenheim expresses himself confidently in regard to a point lying between 250° and 260° at which a marked absorption of heat takes place. In spite of the fact that other observers, including ourselves, had discovered no definite evidence of the existence of such a point, it seemed worth while to investigate this region by means of the dilatometer.

The observations were made with crystallized sulphur which had been melted and treated with ammonia. The same apparatus as before was employed. The inner tube, in which the dilatometer was placed, contained phthalic anhydride. The bath was charged first with diphenyl and, at the higher temperatures, with diphenylmethane. The temperature was varied as before by altering the pressure under which the substance in the outer tube boiled. The readings were made at intervals of 3-5°. The results were as follows:

Cryst. S + NH_3.		Cryst. S + NH_3.	
Mean temp.	Expansion for 1°.	Mean temp.	Expansion for 1°.
222.6	13.3	247.9	13.5
227.6	13.4	252.7	13.6
234.5	13.1	258.1	13.5
239.6	13.1	262.9	13.8
243.7	13.2		

There was thus no evidence of any change in the dilatation between 220° and 266°.

VI. DIRECT OBSERVATION OF THE SEPARATION INTO TWO PHASES.

When pure, redistilled sulphur is melted in a test-tube and heated until it becomes viscous the separation into two phases is easily observed as the liquid cools. In consequence of the relatively greater surface of the bottom of the tube and the more rapid loss of heat at this place, the lowest part of the sulphur is the first to pass into the pale yellow form. The interface between this portion and the dark brown material above is at first very distinct. It recedes gradually up the tube, but soon vanishes in consequence of the progress of the transformation within the upper layers themselves and the gradual increase in mobility and decrease in depth of color in this region. If the tube is kept in a bath

at 158-160° the upward movement of the interface can be followed for a much longer time.

It was thought, at first, that a method of determining the temperature of the transition might be founded upon this, by varying the temperature of the bath until a point was discovered at which the interface remained constantly in the same position. But it was found that, even at temperatures very little below the transition point, the change went on within each mass, as well as at the interface, so that the sharpness of the plane of demarkation could not be maintained for a sufficient length of time.

RESULTS OF THIS INVESTIGATION.

(1) With melted rhombic sulphur the appearance of easily perceptible viscosity takes place first at 159.5°.

(2) The absorption of heat connected with the transition occurs at 162.5° and upwards, and the liquid becomes viscous at the same moment. The temperature falls to 162°, and the transition is therefore not higher than this temperature.

(3) Distilled sulphur does not show any sharp onset of viscosity or noteworthy absorption of heat and appears therefore to be more subject to superheating than is recrystallized sulphur.

(4) These phenomena take place in the same way and at precisely the same temperature whether the sulphur concerned is such as by chilling gives insoluble sulphur or, having been treated with ammonia, does not.

(5) The existence of two independent curves of solubility for the two kinds of liquid sulphur in triphenylmethane and other solvents is demonstrated. The solubility of yellow mobile sulphur (S_λ) increases; that of brown viscous sulphur (S_μ) decreases with rise in temperature.

(6) The expansion of yellow mobile sulphur (S_λ) diminishes rapidly from 154° to 160°; that of brown, viscous sulphur (S_μ) increases rapidly from 160° upwards. The statement under (4) holds in this case also.

(7) The coefficients of expansion of sulphur for short intervals of temperature from 154-170°, covering the regions on each side of the transition, are determined.

(8) The dilatometric method gives no evidence of the existence of Frankenheim's transition point (250-260°).

(9) It is shown that the point of minimum dilatation is displaced upwards when triphenylmethane is dissolved in the sulphur. The displacement averages 2.8° for 1 per cent. of this foreign body.

(10) An experiment is described in which the separation of the two phases, yellow and brown liquid sulphur, may be observed.

(11) It is thus shown conclusively that there are two liquid states of sulphur which are partially, but only partially, miscible. These are S_λ, which predominates from the melting-point to 160°, and S_μ, which prevails above 160°. As the temperature ascends, saturation of the former with the latter determines the separation of the new phase, and conversely when the temperature falls.

REACTIONS IN LIQUID AMMONIA.[1]

BY EDWARD CURTIS FRANKLIN.

Received May 2, 1905.

INTRODUCTION.

THE striking parallelism between the general properties of liquid ammonia and water has been emphasized by the writer and his co-workers in previous papers.[2] Water, among solvents, is characterized by its high boiling-point, its high specific heat, its high heat of volatilization and heat of fusion, its high critical temperature and pressure, its high association in the liquid condition, its high dielectric constant, by its low boiling-point elevation constant, by its power to unite with salts as water of crystallization, by its wide solvent power, and by the fact that, with the possible exception of hydrocyanic acid, it is the most powerful ionizing solvent known. Aqueous solutions of salts are also, generally excellent conductors of electricity.

Of all well-known solvents ammonia most closely approaches water in all those properties, which give to the latter its unique position among solvents. While the boiling-point of liquid ammonia is 33.6° below zero, it still appears abnormally high when compared with the boiling-points of such substances as methane, ethylene, hydrogen sulphide, phosphine, arsine, hydrochloric acid,

[1] Presented in abstract at the Philadelphia Meeting of the American Chemical Society.

[2] Franklin and Kraus: *Am. Chem. J.*, **20**, 820 and 836 (1898); **21**, 8 (1899); **23**, 277 (1900); Franklin and Stafford: *Ibid.*, **28**, 83 (1902).

etc.[1] The specific heat of liquid ammonia and the heat of fusion of the solid are greater than the corresponding constants for water, while its heat of volatilization, with the one exception of water, is the highest of any known liquid. Its critical temperature is abnormally high, while its critical pressure, the more characteristic constant, is higher than that of any other liquid, excepting water. Ammonia is an associated liquid, and its dielectric constant, while much below that of water, is still high. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3.4, as compared with 5.2 for water, and it quite equals, or even exceeds, water in its power to unite with salts as ammonia of crystallization. As a solvent for salts it is inferior to water, though some salts, for example, silver iodide, dissolve much more abundantly in ammonia than they do in water, and it far surpasses the latter solvent in its power to dissolve the compounds of carbon. Finally, it exhibits very marked power as an ionizing solvent, the more dilute ammonia solutions being even better conductors of electricity than aqueous solutions of the same concentration.

It is perhaps well to add that, contrary to the behavior of water, liquid ammonia does not show a maximum density above its freezing-point.

METATHETIC REACTIONS BETWEEN ORDINARY SALTS, ACIDS AND BASES IN LIQUID AMMONIA.

Reactions between Salts.—The general resemblance between ammonia and water, outlined above, led Franklin and Kraus to inquire whether the ordinary metathetic reactions take place in the former solvent as they do in the latter. This was found to be the case,[2] with the interesting difference that, as a result of variations in the order of solubilities in ammonia as compared with water, many reactions take place in the former solvent, which do not occur in the latter, or they may even proceed in opposite directions in the

[1] The abnormally high boiling-point of liquid hydrofluoric acid, its evident association, even in the gaseous state, its power of uniting with fluorides, and the fact that Moissan has found a hydrofluoric acid solution of potassium fluoride to be a good conductor of electricity, are considerations which have led the writer to suspect that hydrofluoric acid is to be classed with water and liquid ammonia as an excellent electrolytic solvent.

Some preliminary experiments on hydrofluoric acid have shown it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, sodium nitrate, sodium chlorate, potassium bromate, acetamide, urea, and potassium sulphate are abundantly soluble; silver cyanide, barium fluoride, and copper chloride appear to dissolve to some extent, while calcium fluoride, copper sulphate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride, and metallic magnesium are insoluble.

[2] *Am. Chem. J.*, **21**, 1 (1899).

two solvents. As examples, may be mentioned the separation of the sulphides of the alkaline earth metals as white precipitates, when solutions of soluble salts of these metals and ammonium sulphide are brought together, and the precipitation of calcium chloride when solutions of sodium chloride and calcium nitrate are mixed.

Reactions between Bases and Acids.—So far as such compounds have been tested, no metallic oxides or hydroxides are soluble in liquid ammonia. On the other hand, many acids, both oxygen acids and halogen acids, as a matter of course in the form of their ammonium salts,[1] dissolve freely in ammonia to form solutions which exhibit certain truly acid properties, as follows: First, they discharge the color of an ammonia solution of phenolphthalein, which has been rendered alkaline[2] by the addition of a small quantity of a base. Second, solutions of ammonium salts in ammonia dissolve sodium, potassium, calcium and magnesium with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation, $M + NH_4X = MX + NH_3 + H$. Third, many metallic oxides and certain basic salts, all the members of both classes of compounds being insoluble in ammonia, dissolve in solutions of ammonium salts. For example, Divers found sodium hydroxide, potassium hydroxide, and the oxides of cobalt, copper, lead, magnesium, mercury, cadmium, and zinc to be soluble in ammonia solutions of ammonium nitrate, while the writer has confirmed these results, and has also observed the solubility of potassium hydroxide in solutions of ammonium salts other than the nitrate. It therefore, appears, that bases dissolve in ammonia solutions of ammonium salts in a manner analogous to the solution of insoluble bases in aqueous acid solutions as indicated by the equations:

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$
$$CaO + 2NH_4NO_3 = Ca(NO_3)_2 + H_2O + 2NH_3.$$

Even in water solutions what may be called the acid properties of ammonium salts are sometimes in evidence, as, for example, in

[1] Note: The acid properties of ammonia solutions of ammonium salts suggest that, analogously, in water solutions, the hydrogen ion may be associated with water as $\overset{+}{O}H_3$.

[2] It seems hardly necessary to emphasize the fact that the compound ammonia is not a base, and that, consequently, it is not surprising that the dry liquid has no effect upon phenolphthalein other than to dissolve it.

the solution of magnesium hydroxide and the mercuri-ammonium compounds in aqueous solutions of ammonium salts.

REACTIONS IN LIQUID AMMONIA BETWEEN COMPOUNDS RELATED TO AMMONIA AS THE ORDINARY OXYGEN SALTS, ACIDS, AND BASES ARE RELATED TO WATER.

Nomenclature.—In order to distinguish by name between the oxygen salts, acids and bases on the one hand, and those compounds which bear to ammonia relations analogous to those which salts, acids and bases bear to water on the other, the writer ventures to refer to the water derivatives as hydro-salts, hydro-acids and hydro-bases, and to offer for general use the names, ammono-salts, ammono-acids and ammono-bases, for the corresponding ammonia derivatives.

Potassium nitrate, calcium sulphate and sodium acetate are accordingly hydro-salts; potassium hydroxide and calcium oxide, hydro-bases; and acetic acid and sulphuric acid, hydro-acids; while potassium acetamide, sodium succinimide, sulphamide and mercury urea are ammono-salts; sodium amide, lead imide and mercuric nitride are ammono-bases; and acetamide, carbamide, succinimide and picramide are ammono-acids.

The relations of the halogen acids and salts and of the sulpho-acids and sulpho-salts to ammonia are quite the same as their relations to water, with the exception, of course, that the acids in solution in ammonia are present as the ammonium salts.

Ammono Salts.—The obvious parallelism between water and its derivatives, the bases, acids and salts on the one hand, and ammonia with its family of derivatives, the metallic amides, the acid amides, and the ammono-salts on the other, led the writer, collaborating with Mr. O. F. Stafford, to study in some detail the reactions beween the acid and basic amides in ammonia solutions.[1] The result of this work was to show that the acid amides, which discharge the red color of an alkaline solution of phenolphthalein in liquid ammonia, react with the soluble metallic amides, which give the characteristic red color with the same indicator, to form metallic derivatives of the acid amides in a manner analogous to the familiar reaction between acids and bases in water solutions.

[1] *Am. Chem. J.*, **28**, 83 (1902).

For example, acetamide, an ammono-acid and potassium amide, an ammono-base, react with each other in ammonia solutions to form potassium acetamide, an ammono-salt, as follows:

$$CH_3CONH_2 + KNH_2 = CH_3CONHK + NH_3,$$
$$CH_3CONH_2 + 2KNH_2 = CH_3CONK_2 + 2NH_3,$$

and urea, the ammonia analogue of carbonic acid reacts with potassium amide to form potassium carbamide.

$$CON_2H_4 + KNH_2 = CON_2H_3K + NH_3$$
$$CON_2H_4 + 2NH_2K = CON_2H_2K_2 + 2NH_3.$$

Such of these ammono-salts as are soluble should, if the analogy between these compounds and the hydro-salts is to hold, give solutions which are good conductors of electricity. Only one such compound has so far been tested in this respect. Franklin and Kraus have found the solution of mercury succinimide to be an excellent conductor.[1]

Ammono-Salts Analogous to the Plumbates, Aluminates, Etc.—Certain metallic derivatives of ammonia, the silver, aluminum, copper and lead compounds, for example, dissolve in excess of potassium amide just as many metallic hydroxides and oxides dissolve in aqueous solutions of potassium hydroxide. The compounds formed are presumably related to ammonia as potassium aluminate, for example, is related to water. Up to the present, attempts have been made to isolate but one of these compounds. An analysis of an impure specimen of the lead derivative gave results roughly approximating the formula $PbNK.NH_3$ or $PbNH_2NHK$.[2]

Other compounds belonging to the class of ammono-salts are probably to be prepared by the action of metallic potassium or of potassium amide upon the non-metallic[3] amides and imides, and perhaps even by the action of potassium amide upon the nitrides. A study of this class of reactions is now in progress in this laboratory.

Ammono-Bases (*Metallic Amides, Imides and Nitrides*).—As among the hydro-bases, the hydroxides of the alkali metals only are soluble to any considerable extent in water, so with the ammono-

[1] This Journal, **27**, 191 (1905).
[2] See p. 843.
[3] See p. 826.

bases, it is the amides of the alkali metals which are soluble in ammonia. Indeed, potassium amide only (perhaps also rubidium and caesium amides) among the ammono-bases is abundantly soluble in ammonia. Taking advantage of the solubility of potassium amide the writer has been able to prepare a number of insoluble metallic derivatives of ammonia by bringing soluble metallic salts and potassium amide together in ammonia solution. The new substances are thus obtained as precipitates which may be purified and analyzed, and their identity thereby established. For example, potassium amide reacts with silver nitrate to form silver amide, with lead nitrate or iodide to form lead imide, and with mercuric iodide and bismuth iodide to form mercuric nitride and bismuth nitride respectively. These reactions are represented by the following equations, which are seen to be entirely analogous to the equations representing the formation of the insoluble hydroxides and oxides from aqueous solutions:

$$AgNO_3 + KNH_2 = AgNH_2 + KNO_3,$$
$$Pb(NO_3)_2 + 2KNH_2 = PbNH + 2KNO_3 + NH_3$$
$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$$
$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3.$$

The new bases thus obtained are insoluble in ammonia, but dissolve readily in ammonia solutions of ammonium salts, and are decomposed by the action of water with evolution of ammonia. The four above enumerated are very explosive.

The soluble members of the group of metallic amides form solutions which are good conductors of electricity and which produce color changes in ammonia solutions of various indicators in a manner analogous to the action of bases in aqueous solution.

Ammono-Acids (Acid Amides, Imides and Nitrides).—The acid amides and imides derived from the organic acids constitute a very well-known group of compounds, practically every known carboxylic and sulphonic acid furnishing such a derivative. The amides of the inorganic acids are not so well known, although in recent years several such compounds have been prepared and studied,[1] among others, especially the amides of sulphuric and nitric acids. The members of the large group of ammono-acids,

[1] Traube: *Ber. chem. Ges.*, **25**, 2472 (1892); **26**, 610 (1893); Hantzsch and Holl: *Ibid.*, **34**, 3435 (1901); Ruff: *Ibid.*, **36**, 2900 (1903); Thiele and Lachman: *Ann. Chem.* (Liebig), **288**, 267 (1895); Franklin and Stafford: *Am. Chem. J.*, **28**, 95 (1902); Franklin and Kraus: This Journal, **27**, 191 (1905).

in so far at least as they are soluble, give solutions in liquid ammonia which discharge the color of alkaline solutions of phenolphthalein, which conduct the electric current—though some of them, it must be remembered, are very poor conductors—and which react with metallic amides to give representatives of the class of ammono-salts.

A further class of compounds which are properly included among the ammono-acids are the amides, imides and nitrides of the non-metallic elements. Just as the halogen derivatives of the strongly electro-negative elements, such as arsenic, phosphorus, boron, silicon, etc., are completely hydrolyzed by the action of water, so one would expect the same compounds to undergo complete decomposition in liquid ammonia, with the formation of compounds bearing relations to this solvent analogous to those which the hydrolytic products bear to water.

The following equations giving the results of recent work show that such action takes place:

$$TeCl_4 + 5NH_3 = Te_3N_4 + 4NH_4Cl,^1$$
$$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH,^2$$
$$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl,^3$$
$$PCl_3 + 5NH_3 = P(NH)NH_2 + 3NH_4Cl,^4$$
$$AsCl_3 + 6NH_3 = As(NH_2)_3 + 3NH_4Cl,^5$$
$$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl,^6$$
$$SiS_2 + 4NH_3 = Si(NH)_2 + 2NH_4SH,^7$$
$$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 4NH_4Br.^8$$

Another class of ammono-acids is represented by picramide,[9] trinitraniline, a compound related to ammonia as picric acid is to water. Ammonia solutions of picramide are excellent conductors of electricity.

Ammono-Basic Salts (*Ammonolysis*).—The above-cited reactions in their relation to ammonia are strictly analogous to the

[1] Metzner: *Compt. Rend.*, **124**, 32 (1897).
[2] Stock and Pappenberg: *Ber. chem. Ges.*, **34**, 399 (1901).
[3] Joannis: *Compt. Rend.*, **135**, 1106 (1903).
[4] Joannis: *Ibid.*, **130**, 364 (1904).
[5] Hugot: *Ibid.*, **139**, 54 (1904).
[6] Lengfeld: *Am. Chem. J.*, **21**, 531 (1899); Vigouroux and Hugot: *Compt. Rend.*, **136**, 1670 (1903).
[7] Blix and Wirbelauer: *Ber. chem. Ges.*, **36**, 4220 (1903).
[8] Blix: *Ibid.*, **36**, 4219 (1903).
[9] *Am. Chem. J.*, **28**, 102 (1902); This Journal: **27**, 197 and 215 (1905).

reactions which take place when the respective substances are treated with water. Such reactions are, therefore, appropriately designated as ammonolytic in order to recall their close relation to hydrolytic reactions. These ammonolytic reactions proceed energetically to completion just as do the corresponding reactions with water. On the other hand, as the well-known hydrolytic reactions between certain salts and water are reversible, so also many salts of mercury, lead, bismuth, and aluminum, when treated with liquid ammonia, have been found to give precipitates,[1] which are increased in amount by the addition of an ammono-base, and which are completely dissolved by the addition of an ammonium hydro- or halogen salt or of an ammono-acid. For example, when mercuric chloride, mercuric iodide, and lead iodide are treated with liquid ammonia, the following reversible equations have been found to express their respective behavior.

$$HgCl_2 \rightleftarrows 2NH_3 = NH_2HgCl + NH_4Cl$$
$$2HgI_2 + 4NH_3 \rightleftarrows HgNHgI + 3NH_4I^2$$
$$2PbI_2 + 6NH_3 \rightleftarrows Pb(NH_2)_2.NH_2PbI + 3NH_4I$$

The ammono-basic salts NH_2HgCl, $Pb(NH_2)_2.NH_2PbI$, and Hg_2NI, appear as solid phases while the remaining components of the system constitute the liquid phase. The analogy between these reactions and the ordinary hydrolytic reactions is obvious.

THE MERCURI-AMMONIUM COMPOUNDS.

Most ammono-bases and ammono-basic salts, in the presence of water, are completely hydrolyzed into hydro-bases or hydro-basic salts and ammonia. Many mercury compounds and a few silver compounds are, however, exceptions to this rule. Especially are ammono-basic salts of mercury capable of existence in the presence of water, and as a consequence, many such compounds have been long known and are described in the literature as the mercuri-ammonium compounds.[3]

The action of ammonia on mercuric oxide and mercuric salts gives rise to a large group of substances upon the constitution

[1] Cf. Franklin and Cady: This Journal, **26**, 512 (1904).

[2] Francois (*Compt. Rend.*, **130**, 332 (1900)) has found the equation $HgI_2+4NH_3+H_2O=Hg_2NI.H_2O+4NH_4I$ to be reversible in aqueous ammonia solution.

[3] "Handb. anorg. chem." (Dammer), Vol. II, p. 896 (1894), and Vol. IV, p. 630 (1903); "Handwörterb. Chem." (Fehling), Vol. V, p. 1091 (1890); "Handworterb. Chem." (Ladenburg), Vol. X, p. 148 (1892); "Dict. Chem." (Watts), Vol. III, p. 208 (1892).

of which the most diverse opinions have been expressed. Kane[1] showed some sixty years ago that the earlier assumption that the compounds of mercuric oxide and mercuric salts with ammonia are simple addition products, is in some cases obviously wrong, for, while certain of these compounds may be so constituted, his analyses of the infusible white precipitate showed it to have the composition $HgClNH_2$. As a result of his investigations he proposed his amide theory, which for a time found considerable favor, but which was later, on the authority of A. W. Hofmann,[2] and especially of Rammelsberg,[3] replaced by the ammonium theory, according to which these compounds are considered to be ammonium hydroxide or ammonium salts in which hydrogen is replaced by mercury. While in recent years the ammonium theory has been declared inadequate[4] to explain the behavior of the group of compounds to which the infusible white precipitate belongs, it still finds a vigorous defender in Professor Pesci.[5]

The writer proposes to reject the ammonium theory entirely as applied to the so-called mercury ammonium compounds, and to return to the amide theory of Kane, modified to suit modern requirements, as best adapted to explain the formation and behavior of these compounds. Accordingly all the mercuri-ammonium compounds described in the literature may be classified under the three heads: first, ammono-basic salts; second, mercuric salts with ammonia of crystallization; and third, mixed hydro- and ammono-basic compounds.

I. *Ammono-Basic Salts.*—The best known representative of this class of compounds is the infusible white precipitate which

[1] *Ann. Chem.* (Liebig), **18**, 135 and 288 (1836); *Pogg. Ann.*, **42**, 368 (1837); *Ann. chim. phys.*, **72**, 342 (1839).

Note: In the latter paper Kane makes the following remarks which are significant in the present connection:

"— — " L'amidogène NH_2 peut se combiner avec les méteau; les amides métalliques ont une tendence singulière a se combiner avec les chlorures ou oxides du meme métal ou d'un métal de la meme famille, et a former ainsi des corps qui ressemblent aux oxichlorures, aux sulfochlorures et aux oxisulfures."

" — — $NH_3 = NH_2 + H$. amidide d'hydrogène peut remplir des memes fonctions que l'eau, oxide d'hydrogène, soit comme une eau basique, soit comme eau de cristallisation; il peut également remplacer l'eau, a laquelle Graham a donné le nom d'eau saline, dans certaines sels."

[2] *Jahresber.*, 1856, p. 408.

[3] *J. prakt. Chem.*, **146**, 563 (1888).

[4] Hofmann and Marburg: *Ann. Chem.* (Liebig), **305**, 198 (1899); *Z. anorg. Chem.*, **23**, 126 (1900).

[5] *Z. anorg. Chem.*, **21**, 361 (1899).

is found in the literature variously formulated as mercuri-ammonium chloride, $Hg:NH_2\text{-}Cl$;[1] as dimercuri-diammonium chloride, $N_2H_4Hg_2Cl_2$;[1] as a double salt of dimercuri-ammonium chloride and ammonium chloride, $NHg_2Cl.NH_4Cl$;[2] and as mercuric chloramide,[3] $NH_2.HgCl$.

The writer's investigations show that the infusible, white precipitate and its related compounds are to be looked upon as ammono-basic salts; that is, they are compounds related to ammonia as the ordinary hydro-basic salts are to water. The infusible, white precipitate is accordingly $NH_2\text{-}Hg\text{-}Cl$, while the so-called dimercuri-ammonium salts are to be given the general formula, $Hg:N\text{-}Hg\text{-}X$, where X is any acid radical.

II. *Mercuric Salts with Ammonia of Crystallization.*—The fusible white precipitate, together with the corresponding mercuric bromide and mercuric iodide compounds, all of which are formed by the direct addition of ammonia to the respective salts, are to be included in the large class of compounds, which are properly described as salts with ammonia of crystallization. The fusible precipitate is, therefore, to be formulated as $HgCl_2.2NH_3$, and not as a double salt of dimercuri-ammonium chloride and ammonium chloride, $NHg_2Cl.3NH_4Cl$,[4] nor yet as mercuri-diammonium chloride, $Hg(NH_3)_2Cl_2$,[5] although, to be sure, this latter formula may possibly represent the manner in which ammonia of crystallization is combined.

III. *Mixed Hydro- and Ammono-Basic Compounds.*—In this class are to be included all the numerous mercury ammonia compounds containing oxygen, every one of which may be formulated as compounds containing residues basic both to water and ammonia. One of the simplest members of the class is the compound $2HgO.NH_3$, which is made by the direct action of ammonia on mercuric oxide. The evidence in favor of any one of the formulas, $2HgO.NH_3$, $HgO.HgNH.H_2O$, $Hg:N\text{-}Hg\text{-}OH.H_2O$, $Hg(OH)_2.HgNH$, $NH_2\text{-}Hg\text{-}O\text{-}Hg\text{-}OH$, or $HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}OH$, which represent the substance as a mixed hydro-basic and ammono-basic compound, seems quite as good, even much better, than

[1] "Dict. Chem." (Watts), Vol. III. p. 208 (1892).

[2] Rammelsberg: *J. prakt. Chem.*, **146**, 588 (1888); Pesci: *Loc. cit.*; Dammer's "Handbuch," *Loc. cit.*

[3] Kane: *Ann. Chem.* (Liebig), **18**, 135 and 288 (1836); Hofmann and Marburg: *Loc. cit.*

[4] Rammelsberg: *Loc. cit.*; Pesci: *Loc. cit.*

[5] Hofmann and Marburg: *Loc. cit.*

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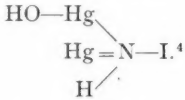
any the writer has been able to find in the literature in support of the formula $NHg_2\text{-}OH.H_2O$,[1] for hydrated dimercuri-ammonium hydroxide, of the formula $NH_2(HgOHg)\text{-}OH$,[2] for oxydimercuri-ammonium hydroxide, or of the formula $(NHg_2)_2O.3H_2O$, which is included in Dammer's "Handbuch der anorganischen Chemie"[3] among the dimercuri-ammonium hydroxides.

Another member of this group, which has often been the subject of investigation, is the compound $2HgO.NH_3.H_2O$, usually called Millon's base, although sometimes considered to be the hydrate of the base. There are to be found in the literature at least six different formulas for this compound, $2HgO.NH_3.H_2O$, $NH_2(HgOHg)OH.H_2O$, $(HOHg)_2NH_2\text{-}OH$, $(NHg_2)_2O.5H_2O$, $NHg_2OH.2H_2O$, and $\begin{matrix}HgNH_2\\HgNH_2\end{matrix}\!\!>\!O.2HgO$, in each of which, with the exception of the first, the substance is formulated as a mercuri-ammonium compound. Of the numerous possible formulas representing the compound as a mixed mercury derivative, basic both to ammonia and water, it is probably best to write simply, $2HgO.NH_3.H_2O$, or possibly, $Hg(OH)_2.HOHgNH_2$ or $3Hg(OH)_2.Hg(NH_2)_2$.

Another important member of this group is Nessler's precipitate, which is usually considered to be the iodide of Millon's base. The writer maintains that the formula $NH_2\text{-}Hg\text{-}O\text{-}Hg\text{-}I$, which represents the compound as a mixed ammono-basic and hydrobasic mercuric iodide, describes the formation and behavior of Nessler's precipitate much better than does its formulation as oxydimercuri-ammonium iodide, $NH_2(HgOHg)J$,[4] or as hydrated dimercuri-ammonium iodide, $NHg_2I.H_2O$,[4] or as hydrated tetramercuri-ammonium iodide, $N_2Hg_4I_2.2H_2O$,[5] or yet as



EXPERIMENTAL.

The experiments described below were made to determine whether new metallic amides, imides or nitrides might be made by metathetic reactions between a soluble basic amide, potassium

[1] "Dict. Chem." (Watts), Vol. III, p. 209 (1892).
[2] "Handwörterb Chem." (Ladenburg): Vol. X, p. 155 (1892).
[3] Vol. II 2, p. 897 (1894).
[4] "Dictionaries of Chem."
[5] Francois: *Compt. Rend.*, **130**, 571 (1900).

amide, and salts of other metals in solution in liquid ammonia.

Preparation of Potassium Amide.—The potassium and sodium amides used in the previous work of the writer and his collaborators were made by the action of pure liquid ammonia on the metals,[1] the blue solution of the metals thus formed changing gradually in the course of hours, days, or even months, into solutions of the metallic amides in accordance with the equation $M+NH_3=MNH_2+H$.

During the earlier stages of the work described in these pages it was noticed that in certain tubes containing bits of asbestos fiber, from the filters introduced into the tubes, that the time-consuming operation of preparing the potassium amide was very markedly shortened in a number of cases. This suggested the use of some catalyzing agent to accelerate the reaction, which was soon found in spongy platinum and oxide of iron.[2]

Method of Manipulation.—The nature of the solvent and of the metallic amides rendered necessary the adaptation of special methods of procedure which are herewith described.

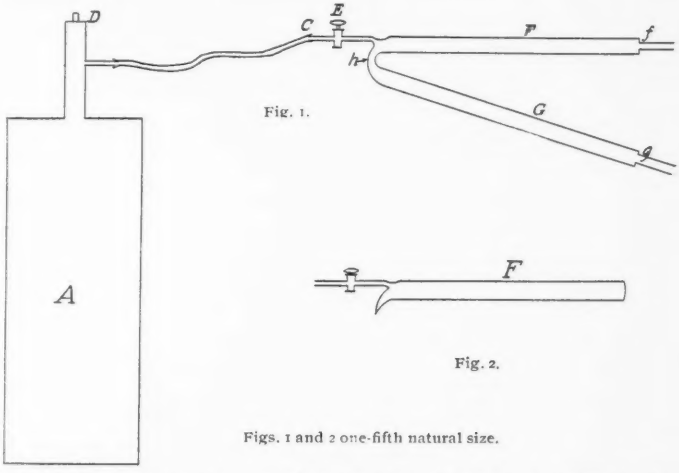


Fig. 1.

Fig. 2.

Figs. 1 and 2 one-fifth natural size.

[1] Joannis: *Compt. Rend.*, **112**, 392 (1891); Franklin and Stafford: *Am. Chem. J.*, **28**, 83 (1902).

[2] It had been a matter of surprise to Franklin and Kraus during their attempts to measure the conductivity of sodium and potassium solutions to find the metal disappear so rapidly from their solutions. They also noticed that large quantities of metallic sodium introduced into the steel supply cylinders were completely transformed into sodium amide in a short space of time. The presence of platinum black on the electrodes and of ferric oxide in the cylinder account for the rapid action. *Am. Chem. J.*, **23**, 306 (1900); *Ibid.*, **24**, 91 (1900).

A is a steel cylinder containing purified ammonia, perfectly dried by the introduction of metallic sodium into the cylinder.[1] *F G* is the reaction tube which is attached to the exit of the ammonia container by means of small lead tubing and elastic sealing-wax, as first used by Joannis. After connection has thus been made, a slow current of ammonia is allowed to pass through the legs *F* and *G*, which are kept hot by means of a Bunsen flame, until the reaction apparatus is completely dried. With *f* closed by means of a stopper, and a current of ammonia gas escaping at *g*, a quantity of clean, unoxidized potassium is introduced into *G*, together with a few milligrams of spongy platinum. The leg *G* is then sealed off at *g*, the end blown out symmetrically and annealed to lessen the danger of explosion from the pressure, which is later developed within the tube. The shaping of the closed end of the tube is accomplished by closing momentarily the opening *f* by means of the finger. The salt is then introduced into the leg *F*, heated in a current of ammonia if necessary to insure perfect drying, and the opening *f* is closed, as has just been described, the pressure necessary for "blowing" the end *f* being obtained by removing the plug from the stop-cock *E* and closing the opening with thumb and finger. The leg *G* is now placed in ice-water and the stop-cock *E* and valve *D* are opened until the leg is about one-fourth filled with liquid, which distils over rapidly from the stock cylinder. The presence of the spongy platinum so greatly accelerates the action of the metal on the ammonia that as much as a gram of potassium will be converted into potassium amide in the course of some fifteen minutes. When the reaction is completed and the hydrogen has been allowed to escape through *E* the valve *D* is again opened and ammonia, sufficient to nearly half fill both legs, is distilled into the apparatus. The lead tube is then disconnected at *C*. When the salt in *F* is dissolved and the two solutions are homogeneous, potassium amide solution is poured from *G* into the salt solution in *F*. The precipitate, after thorough mixing with the solvent, is allowed to settle, after which the solution is poured from the precipitate into the arm G. The ammonia is then distilled completely from *G* into *F* by immersing *G* in luke-warm water and *F* in ice-water. The tube is shaken to thoroughly mix the precipitate with the wash liquid, the precipitate is allowed to settle, and the supernatant liquid is poured back

[1] Franklin and Kraus: *Am. Chem. J.*, **23**, 285 (1900).

into *G*. This operation is repeated as many times as may be necessary for the complete washing of the precipitate. The liquid is then allowed to evaporate slowly through *E*, after which the tubes are sealed apart at *h*. In case the precipitate is very explosive the two arms are cooled off in a bath of liquid ammonia and the separation at *h* made with the precipitate protected by a covering of liquid ammonia inside the tube. The leg *F*, containing the washed and dried substance, and having now the form shown in Fig. 2, is attached to the mercury pump and evacuated, then detached and weighed. After removing the contents the tube is again evacuated and weighed, thus giving the weight of the substance for analysis. When it is desired to pour the salt solution into the solution of potassium amide a three-legged tube is used as follows:

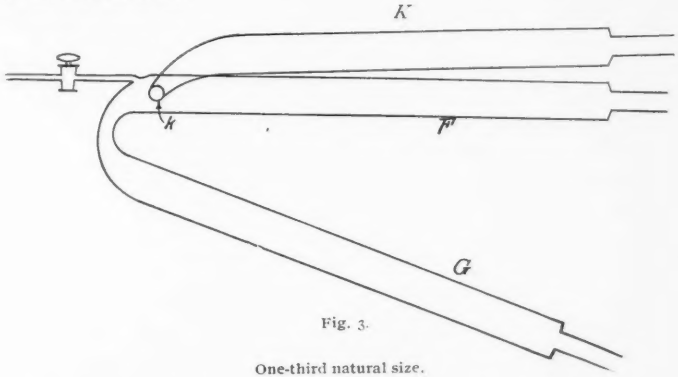


Fig. 3.

One-third natural size.

Metallic potassium and platinum sponge are introduced into the leg *K*, and the salt into *G* as described above. After the conversion of the metal into the amide the solution is poured from the platinum sponge and bits of glass into *F* and the third leg *K* is sealed off at *k*. The further operations are then carried on as described above.

RESULTS.

Silver Amide, $AgNH_2$.—When a solution of potassium amide is run into an excess of silver nitrate solution a pure white precipitate separates which settles fairly well and hence may be washed by the decantation method described above. To avoid the certainty of explosion, which follows, all attempts to separate the two arms

of the preparation tube after the silver amide is dried, the arm *F* containing the precipitate protected by a deep layer of liquid ammonia, is immersed in a bath of liquid ammonia to reduce the internal pressure to that of the atmosphere. The stop-cock *C* is then opened and the preparation tube sealed apart at *h*, after which the liquid in *F* is allowed to evaporate very slowly through the stop-cock *C*, and the residual gas is removed by exhaustion on a Sprengel pump. To remove the product for analysis the tube is held in a clamp and a small quantity of dilute sulphuric acid is allowed to enter in such a manner as not to come into direct contact with the amide. The tube is then allowed to stand until the amide is decomposed and has lost its explosive properties. The residue is then brought into contact with the dilute acid and the solution thus formed removed for analysis. The ammonia was determined by the usual volumetric method and the silver precipitated and weighed as silver chloride.

From some twenty or more attempts to prepare the substance for analysis, the most of which terminated in violent explosions, the following results were obtained:

I. 0.484 gram substance gave 0.0609 gram N and 0.5505 gram AgCl.

II. 0.340 gram substance gave 0.0438 gram N and 0.3849 gram AgCl.

III. 0.300 gram substance gave 0.0382 gram N and 0.3434 gram AgCl.

IV. 0.262 gram substance gave 0.0318 gram N and 0.2992 gram AgCl.

V. 0.549 gram substance gave 0.0617 gram N and 0.6361 gram AgCl.

	Calculated for $AgNH_2$.	Found.				
		I.	II.	III.	IV.	V.
N.....	11.19	12.6	12.9	12.7	12.1	11.2
Ag.....	87.2	85.6	85.3	86.3	86.0	87.4

The results given under I, II, III and IV are from preparations which, in all probability, were not free from adsorbed ammonia, for it was found with preparation V that, after evacuation at laboratory temperature, prolonged pumping, accompanied by gentle heating, removed additional gas from the tube. The tubes containing preparations I and II were not evacuated, but were weighed filled with ammonia gas. It seems unnecessary, however, to give

the details of the corrections for these two analyses, especially as the last three analyses leave no doubt as to the composition of the compound.

The action of potassium amide on silver nitrate in solution in liquid ammonia is therefore represented by the equation

$$AgNO_3 + KNH_2 = AgNH_2 + KNO_3.$$

In order to avoid exposing good analytical balances to danger of destruction from explosion the silver amide in its containing-tube was weighed on an old balance which could not be depended upon to give results nearer than about 2 mg.

Silver amide separates as a pure white, rather bulky, precipitate, which dissolves in solutions of ammonium salts. It is not soluble in excess of silver nitrate, but dissolves readily in excess of potassium amide, a behavior which probably indicates the formation of some such compound as silver potassium amide, AgNHK. The precipitate is darkened by the action of light. On drying, it shrinks very much in bulk and is left in the bottom of the tube in the form of more or less strongly discolored, sometimes black, detached masses, which explode with the greatest violence and upon the slightest provocation. During the course of this work many tubes exploded without assignable cause, shattering the containing tubes and tearing holes in several layers of stout toweling wrapped around the tube for the protection of the operator.

The above analyses were all made on silver amide prepared from silver nitrate. It seems worth while to state, however, that the formation of a precipitate, identical in appearance, by the action of potassium amide on a solution of silver iodide, shows that the reaction between a soluble ammono-base and a soluble silver salt is a general one.

The formation of an explosive substance by the action of *aqua* ammonia on silver oxide was observed by Berthollet[1] over a hundred years ago. Because, however, of the extreme instability of Berthollet's compound its composition is even yet uncertain although Raschig[2] concludes from determinations of the ratio of nitrogen to silver that the compound is to be represented by the formula Ag_3N.

Mercuric Nitride, Hg_3N_2.—Mercuric iodide is abundantly soluble in ammonia, forming a dense colorless solution and leaving

[1] *Crell. Ann.*, **2**, 390 (1788).

[2] *Ann. Chem.* (Liebig), **233**, 93 (1886).

undissolved a small quantity of an ammono-basic iodide, the formation of which is prevented by the addition of ammonium iodide. The dense liquid thus formed, unlike the liquid $HgCl_2.12NH_3$, obtained by Franklin and Kraus,[1] is miscible with ammonia in all proportions. Mercuric bromide is also very soluble in liquid ammonia with the separation of an ammono-basic salt, soluble in ammonium bromide. Like mercuric iodide and unlike mercuric chloride the ammonia addition product of mercuric bromide does not form two liquid phases in the presence of excess of liquid ammonia.

When a solution of mercuric iodide, or bromide, is run into an excess of a solution of potassium amide, a chocolate-colored precipitate is formed, which, on standing, becomes darker in color and changes from a bulky mass into a dense powder, which is easily washed. The precipitate is insoluble in excess of potassium amide, but is converted by an excess of the mercury salt into an ammono-basic salt, as described below. It dissolves readily in ammonia solutions of ammonium salts and in aqueous acid solutions. Dry mercuric nitride is very explosive, but is not so sensitive as is silver amide. It explodes on coming in contact with water and must consequently be removed from the preparation tube with all the precautions described above for removing silver amide. A number of attempts at preparing the compound ended in explosions.

For analysis the compound was dissolved in dilute hydrochloric acid. Mercury was precipitated as the sulphide and the ammonia was separated from the filtrate by distillation with the following results:

I. 0.208 gram substance gave 0.2236 gram HgS and 0.0109 gram N.

II. 0.4755 gram substance gave 0.5145 gram HgS and 0.0233 gram N.

III. 0.4512 gram substance gave 0.4982 gram HgS and 0.0218 gram N.

IV. 0.5254 gram substance gave 0.5730 gram HgS and 0.0244 gram N.

V. 0.5626 gram substance gave 0.0245 gram N.

VI. 0.4714 gram substance gave 0.5180 gram HgS.

[1] *Am. Chem. J.*, **23**, 299 (1900).

VII. 0.5844 gram substance gave 0.6445 gram HgS and 0.0275 gram N.

	Calculated for Hg_3N_2.	Found.						
		I.	II.	III.	IV.[1]	V.	VI.[2]	VII.[2]
Hg.....	95.6	92.8	93.3	95.2	94.4	....	95.6	95.4
N.....	4.46	5.3	4.9	4.8	4.6	4.4	....	4.7

Mercuric nitride therefore separates from ammonia solutions in accordance with the equations:

$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3,$$
$$3HgBr_2 + 6KNH_2 = Hg_3N_2 + 6KBr + 4NH_3.$$

Since contradictory statements are found in the literature concerning the existence of mercuric nitride it seems worth while to insert here a short résumé of previous investigations upon this compound. More than sixty years ago Plantamour[3] prepared a dull brown powder which he assumed to be mercuric nitride, by passing a current of ammonia gas over precipitated mercuric oxide heated to 150°. The substance was not analyzed for the reason that he was unable to free his preparation from considerable quantities of metallic mercury and unchanged mercuric oxide. Plantamour describes mercuric nitride as a dark brown (flohbraun) powder which, when heated in small portions of the size of a mustard seed, detonates with a violence scarcely less than that of nitrogen iodide.

In an abstract of his investigations upon the action of ammonia on mercuric oxide, Hirzel[4] is reported as having made analyses confirming the formula Hg_3N_2 for Plantamour's compound.

Weyl[5] rejects the conclusions of Plantamour and Hirzel to the effect that the product is impure mercuric nitride containing mercury and unchanged mercuric oxide, and insists that the substance is a compound containing oxygen. Weyl reports having obtained the compound Hg_2NOH at 80° to 85°, and $(NHg_2)_2O$ at 100° by the action of ammonia on mercuric oxide.

Much more recently Hofmann and Marburg[6] have heated both Millon's base and mercuric oxide in an atmosphere of ammonia gas and find in each case that the end-product is a loose, dark

[1] Prepared from mercuric bromide.
[2] Direct tests for iodine proved this element to be absent from these preparations.
[3] *Ann. Chem.* (Liebig), **40**, 115 (1841).
[4] *Ibid.*, **84**, 258 (1852).
[5] *Pogg. Ann.*, **121**, 601, and **131**, 524.
[6] *Ann. Chem.* (Liebig), **305**, 204 (1899).

brown, very explosive compound of the formula Hg_2NOH. They were unable to obtain mercuric nitride.

Mercuric Iodo-Nitride, Ammono-Basic Mercuric Iodide, Hg_2NI or *Hg:N-Hg-I*. (Dimercuri-ammonium Iodide.)—When potassium amide solution is added to excess of mercuric iodide in solution in liquid ammonia a reddish yellow precipitate of an ammono-basic mercuric iodide is formed. Special care must be taken to thoroughly mix the contents of the tube and to have mercuric iodide in excess, otherwise the precipitate will be contaminated with mercuric nitride. During the course of the work on this substance it was suspected that the compound Hg_2NI undergoes gradual ammonolysis during the process of washing, thus giving for analysis a mixture containing mercuric nitride or some other compound more basic than Hg_2NI. All the analytical results given below are more or less in harmony with this supposition. However, Analysis V, which was made of a specimen of the basic salt during the preparation of which special care was given to the agitation of the precipitate with an excess of mercuric iodide and to continued and thorough washing, has led to the conclusion that the results of the earlier analyses are probably due to the lack of thorough action of excess of mercuric iodide on the precipitate.

For analysis the substance was digested with dilute hydrochloric acid and metallic zinc to separate the mercury. Ammonia was then distilled off and determined volumetrically while the iodine was recovered by boiling the acidified solution with ferric chloride. The mercury in V was determined electrolytically.

I. 0.7878 gram substance gave 0.6944 gram HgS and 0.0228 gram N.

II. 0.7826 gram substance gave 0.6810 gram HgS, 0.0241 gram N and 0.1720 gram I.

III. 0.4422 gram substance gave 0.0138 gram N and 0.0940 gram I.

IV. 0.8720 gram substance gave 0.0247 gram N and 0.1880 gram I.

V. One-fourth of 1.7463 grams substance gave 0.01183 gram N and 0.1012 gram I. Another fourth of 1.7463 grams substance gave 0.01175 gram N and 0.1003 gram I and 0.3217 gram Hg.

	Calculated for Hg_2NI.	Found.				
		I.	II.	III.	IV.	V.
Hg.....	74.0	75.7	75.1	.....	.....	73.7
N.....	2.6	2.9	3.1	3.1	2.8	2.7
I.....	23.4	.....	22.0	21.3	21.6	23.1

A determination of mercury in 82 mg. of the insoluble residue formed by the action of liquid ammonia on mercuric iodide gave 78 per cent. mercury. There is consequently little doubt that the product of the ammonolysis of mercuric iodide is Hg_2NI.

The compound Hg:N-Hg-I has, therefore, been prepared from ammonia solution in accordance with the equations

$$2HgI_2 + 3KNH_2 = Hg_2NI + 3KI + 2NH_3,$$
$$2HgI_2 + 4NH_3 = Hg_2NI + 3NH_4I.$$

This ammono-basic mercuric iodide is obtained as a dense, litharge yellow powder, which is soluble in ammonia solutions of ammonium salts, and by potassium amide is converted into mercuric nitride. It dissolves readily in aqueous solutions of ammonium iodide and is converted by dilute hydrochloric acid into a mixture of mercuric chloride, mercuric iodide and ammonium chloride. Heated in a closed tube it decomposes freely, but without explosion, yielding a sublimate of metallic mercury and mercuric iodide.

The compound Hg_2NI was first prepared by Weyl[1] by the action of liquid ammonia upon the oxyiodide of mercury, $3HgO.HgI_2$, formed by fusing together mercuric oxide and mercuric iodide in the proportions indicated by the formula. Weyl describes his product as a brown powder which explodes when heated to 130°.

A non-explosive compound of the same formula has been prepared by François[2] by the action of a large excess of aqua ammonia on mercuric iodide. François obtained the anhydrous compound in the form of almost black crystals.

Mercuric Brom-Nitride, Ammono-Basic Mercuric Bromide, Hg_2NBr or *Hg-N-Hg-Br*. (Dimercuri-ammonium Bromide).—When potassium amide solution is added to an excess of solution of mercuric bromide a pure yellow precipitate of an ammono-basic mercuric bromide is formed which soon settles to the bottom of the tube as a dense powder. As first formed the precipitate is always more or less mixed with the brown mercuric nitride which is formed

[1] *Loc. cit.*

[2] *Compt. Rend.*, **130**, 332 and 571 (1900).

at the junction of the two liquids, along with the basic salt, when the two solutions are brought together. When, however, the precipitate is shaken with an excess of mercuric bromide the brown areas disappear, after a time, and the whole precipitate takes on the pure yellow color of the ammono-basic salt. The compound is soluble in ammonia solutions of ammonium salts and in aqueous acid solutions. Potassium amide converts it into mercuric nitride.

For analysis the substance was dissolved in dilute sulphuric acid, from which solution the mercury was separated as sulphide. The filtrate from mercuric sulphide was divided into two parts, from one of which the ammonia was separated by boiling with potassium hydroxide. The bromine was removed from the other half as silver bromide after oxidizing the hydrogen sulphide by means of ferric sulphate.

I. 0.3230 gram substance gave 0.3049 gram HgS. One-half of 0.3230 gram substance gave 0.00558 gram N; the other half gave 0.0570 gram AgBr.

II. 0.9176 gram substance gave 0.8686 gram HgS. One-half of 0.9176 gram substance gave 0.01715 gram N; the other half gave 0.1623 gram AgBr.

	Calculated for Hg_2NBr.	Found.	
		I.	II.
Hg	81.0	81.4	81.7
N	2.8	3.46	3.7
Br	16.2	15.0	15.0

These results, which were obtained from two entirely separate preparations, do not point to a pure compound. The low results for bromine and the slightly high content of mercury may be due to the presence of mercuric nitride formed either when the solutions of mercuric bromide and potassium amide were mixed or later as the result of the ammonolysis of the basic compound during the process of washing the precipitate for analysis. The high results for nitrogen may perhaps be accounted for by the presence of adsorbed ammonia. Both specimens were dried *in vacuo* at laboratory temperature.

Notwithstanding these rather unsatisfactory results, there seems to be but little doubt that an ammono-basic mercuric bromide is

formed by the action of potassium amide upon an excess of mercuric bromide in liquid ammonia solution as follows:

$$2HgBr_2 + 3KNH_2 = Hg_2NBr + 3KBr + 2NH_3.$$

Dimercuri-ammonium bromide has previously been made by the action of aqueous ammonia on mercuric bromide solution.[1]

Mercuric Chloramide, Ammono-Basic Mercuric Chloride, NH_2HgCl. (Infusible white precipitate. Mercuri-ammonium chloride).—When mercuric chloride is brought into contact with liquid ammonia an addition-product having the composition $HgCl_2.12NH_3$[2] is formed, which is but slightly soluble in liquid ammonia.[3] The compound is solid at low temperatures, melts somewhere in the vicinity of 0°, and at temperatures above its melting-point forms a two-phase system with excess of liquid ammonia. At laboratory temperature and pressure the compound $HgCl_2.12NH_3$ loses ammonia and is converted into the well-known fusible white precipitate $HgCl_2.2NH_3$. The action of ammonia on mercuric chloride is accompanied by the formation of a small quantity of a white residue insoluble in liquid ammonia, but readily converted into the liquid $HgCl_2.12NH_3$ in the presence of ammonium chloride. A specimen of the substance, which showed itself to be the well-known infusible white precipitate, NH_2HgCl, was prepared by treating some 25 grams of mercuric chloride with excess of liquid ammonia, pouring the ammonia and heavy liquid $HgCl_2.12NH_3$ from the residue, and washing the latter in the usual manner for analysis.

I. 0.6825 gram substance gave 0.6291 gram HgS; one-half of 0.6825 gram substance gave 0.0194 gram N; the other half gave 0.2000 gram AgCl.

	Calculated for NH_2HgCl.	Found.
Hg	79.7	79.5
N	5.7	5.6
Cl	14.1	14.5

Liquid ammonia, therefore, reacts with mercuric chloride in accordance with the equation

$$HgCl_2 + 2NH_3 \rightleftarrows NH_2\text{-}Hg\text{-}Cl + NH_4Cl,$$

which also represents the behavior of the same salt towards

[1] Pesci: *Gazz. chim. ital.*, **19**, 509.

[2] Franklin and Kraus: *Am. Chem. J.*, **23**, 299 (1900).

[3] The statement of Weyl, *loc. cit.*, to the effect that mercuric chloride is very soluble in liquid ammonia is therefore erroneous.

aqueous ammonia. In liquid ammonia solutions the presence of a small quantity of ammonium chloride prevents the formation of the ammono-basic salt. In aqueous ammonia solution, on the contrary, a large excess of ammonium chloride is necessary to insure a pure precipitate of $HgCl_2.2NH_3$.

Mercuric chloramide is also formed by the action of sodium amide upon excess of mercuric chloride. Neither of these substances dissolves freely in liquid ammonia. The heavy liquid addition-product of mercuric chloride was therefore poured in large excess upon the sodium amide and the mixture allowed to stand several days with occasional shaking. The residue was then washed by the method described above to remove sodium chloride and excess of $HgCl_2.12NH_3$. Excess of sodium amide changes the color of the white product thus obtained to dark brown, a result undoubtedly due to the formation of mercuric nitride.

The analysis of the substance, which was conducted as described above, follows:

1.5847 grams substance gave 1.4915 grams HgS; 22/50 of 1.5847 grams substance gave 0.3778 gram AgCl, and 28/50 of 1.5847 grams substance gave 0.0482 gram N.

	Calculated for NH_2HgCl.	Found.
Hg	79.7	81.4
N	5.6	5.5
Cl	14.1	12.7

Evidently the product was not pure $HgClNH_2$. An admixture of a small quantity of a more basic chloride or of mercuric nitride would not be surprising in view of the nature of the mixture from which the preparation was separated.

The equations:

$$HgCl_2 + NaNH_2 = NH_2\text{-}Hg\text{-}Cl,$$

and

$$3HgCl_2 + 6NaNH_2 = Hg_3N_2 + 6NaCl + 4NH_3,$$

therefore represent the action of sodium amide upon mercuric chloride in ammonia solutions.

Reactions between Lead Nitrate and Potassium Amide.—Lead nitrate dissolves readily in liquid ammonia, forming a milky solution which is cleared up by the addition of a small quantity of an ammonium salt. Addition of potassium amide to this solution

gives a precipitate of a white basic salt. Further quantities of potassium amide increase the amount of the precipitate and at the same time change the color through darker shades of yellow to an orange-red. This orange-colored precipitate which is at first flocculent and voluminous, after a time becomes darker in color and changes into a dense powder. Excess of potassium amide dissolves the precipitate completely with the formation, probably, of lead potassium imide, PbNK, or lead potassium amide. Attempts to isolate the compound thus formed have been made, but so far have not led to satisfactory results, for the reason, principally, that the compound is very soluble in ammonia, and is, therefore, difficult to separate from the solution in a pure form. Lead, nitrogen and potassium determinations on an impure specimen gave results roughly approximating the formula $PbNH_2NHK$ or $PbNK.NH_3$. A second purer specimen of colorless, efflorescent crystals was lost by its violent explosion, which occurred on bringing dilute acetic acid into contact with the compound preparatory to analysis. Further attempts to isolate and analyze this compound will be made.

Reactions between Lead Iodide and Potassium Amide.—When lead iodide is brought into contact with gaseous ammonia no action takes place at the ordinary pressure and temperature. Under increased pressure, however, a white addition-product is formed which dissolves freely in liquid ammonia, leaving behind a white or slightly yellowish precipitate of an ammono-basic salt. Addition of a little ammonium iodide gives a perfectly clear, colorless solution. Potassium amide added to this solution gives, as with lead nitrate, first a precipitate of a white basic salt, which is changed by further addition of the ammono-base into lead imide, which latter then dissolves in excess of potassium amide.

The following equations represent the action of potassium amide upon lead iodide solutions:

$$2PbI_2 + 3KNH_2 = NH_2\text{-}Pb\text{-}NH\text{-}Pb\text{-}I + 3KI + NH_3$$
$$PbI_2 + 2KNH_2 = PbNH + 2KI + NH_3$$
$$PbI_2 + 3KNH_2 = PbNK(?) + 2KI + 2NH_3.$$

Similar equations represent the action of potassium amide upon lead nitrate.

Lead Imide, PbNH.—The preparation of pure lead imide is attended with considerable difficulty, principally for the reason

that the absence of a basic salt cannot be insured by the use of an excess of the precipitant. An excess of potassium amide immediately dissolves the precipitate. A number of attempts were made to prepare lead imide by the action of potassium amide upon lead nitrate in ammonia solution all of which, however, gave products more or less contaminated with basic salt. After the first preliminary experiments, the following results were obtained:

I. 0.5612 gram substance gave 0.7452 gram $PbSO_4$ and 0.0353 gram N.

II. 0.3056 gram substance gave 0.4028 gram $PbSO_4$ and 0.0206 gram N.

III. One-half of 2.0229 grams substance gave 1.0360 grams PbS and 0.0019 gram K_2SO_4.[1] The other half of 2.0229 grams substance gave 0.0672 gram nitrogen and and 0.0486 gram NO_3.

IV. 0.1670 gram substance gave 0.2178 gram $PbSO_4$ and 0.0109 gram N.

V. 0.8930 gram substance gave 0.9432 gram PbS and 0.0533 gram N.

	Calculated for PbNH.	Found.				
		I.	II.	III.	IV.	V.
Pb	93.3	90.7	90.2	88.7	89.2	91.7
N	6.3	6.25	6.75	6.7	6.55	6.0
NO_3	....	....	....	4.8	....	....

In support of the assumption that the low percentage of lead in these preparations is due to the presence of basic salt are the observations that all these preparations were distinctly lighter in color than the lead imide prepared from lead iodide as described below. Futhermore, tests for nitrates in Preparation III showed them to be present to the extent indicated.

After the failure of the above-described attempts to prepare pure lead imide the following procedure was found to give a nearly pure product. Lead iodide solution was added slowly and in small portions at a time to a solution of potassium amide until a considerable quantity of the orange-red precipitate was formed.

[1] 0.0019 gram potassium sulphate is the equivalent of 0.0022 gram or 0.21 per cent. potassium nitrate, the amount left in the lead precipitate after washing.

The contents of the tube were thoroughly agitated, and the precipitate was allowed to stand for twenty-four hours, or more, in contact with the mother-liquor during which time the precipitate took on a darker color and changed to a dense, pulverulent mass. After washing in the usual manner with liquid ammonia, and drying *in vacuo* at laboratory temperature, the following analytical results were obtained:

I. 0.1956 gram substance gave 0.2101 gram PbS.

II. 0.5689 gram substance gave 0.7674 gram $PbSO_4$ and 0.0365 gram N.

	Calculated for PbNH.	Found. I.	Found. II.
Pb	93.3	93.2	92.2
N	6.3	(5.6)[1]	6.4

Iodine was proved, by direct tests, to be absent from both these preparations.

Dry lead imide is obtained by the above process in the form of a dense, amorphous mass of reddish brown color. It explodes violently when heated or on coming in contact with water or dilute acids. After decomposition by the slow action of water vapor it dissolves readily in dilute acetic acid or potassium hydroxide solution.

Ammono-Basic Lead Iodide, $Pb_2N_2H_3I$ or NH_2-*Pb*-NH-*Pb*-*I*, or *Pb* : *N*-*Pb*-*I*.NH_3, *or* *PbNH*.*PbNH*$_2$*I*.—When potassium amide solution is poured upon a solution of lead iodide a precipitate which is orange-red on the upper surface and pure white below is formed at the junction of the two solutions. From the lower side of the mass of precipitate occupying a zone between the two solutions, the white basic iodide gradually falls through the lead iodide solution to the bottom of the tube, while from the upper surface of the precipitate the orange-colored lead imide goes into solution in the excess of potassium amide. Agitation of the tube, so long as the lead iodide is in excess, converts the lead imide into basic salt. The substance is thus obtained as a bulky white precipitate which refuses to settle to a small volume. Thorough washing of the precipitate by decantation is, therefore, a time-consuming operation. On allowing the ammonia to escape, the substance is left in the bottom of the tube in the form of white, detached masses which lose ammonia and change in color through

[1] Large losses of ammonia were known to have occurred.

shades of yellow to a dark brown when the temperature is raised gradually to 200°. Basic lead iodide is soluble in ammonia solutions of ammonium salts, and is converted by potassium amide into lead imide after which further addition of potassium amide dissolves the precipitate to form a potassium derivative, probably of the formula PbNK or NH_2PbNHK, as indicated above. The compound is not explosive.

The following analytical results were obtained:

I. This specimen lost its pure white color and was changed to a lemon-yellow when dried *in vacuo* at 100°. 1.0912 grams of the substance gave 0.8898 gram PbS and 0.0647 gram N.

II. This specimen, dried at laboratory temperature, was yellowish in color, the result probably of loss of ammonia or of an admixture of a small quantity of lead imide. 0.2582 gram of the substance gave 0.2709 gram $PbSO_4$ and 0.0541 gram iodine.

III. This preparation was heated *in vacuo* at gradually increasing temperature to 200° until ammonia was no longer given off. The color of the compound was changed to a dark brown by this treatment. 0.7370 gram of the white compound, on heating to 200°, lost 0.0252 gram NH_3. Calculated for the loss of one molecule of ammonia from $Pb_2NI.2NH_3$, 2.9 per cent. Found, 3.4 per cent. 0.6758 gram of the substance, after heating to 200°, gave 0.7185 gram $PbSO_4$ and 0.0332 gram N.

	Calculated for		Found.		
	$Pb_2NI.NH_3$.	$Pb_2NI.2NH_3$.	I.	II.	III.
Pb	72.4	70.3	70.8	71.7	72.8
N	4.9	7.1	5.9	.....	4.9
I	22.2	21.6	.....	20.9	.....

The white substance is, therefore, probably the compound $Pb_2NI.2NH_3$. There can be no doubt that the formula $Pb_2NI.NH_3$, or better perhaps $NH_2PbNHPbI$, represents the composition of the dark brown compound formed by heating the white salt to 200° *in vacuo*.

Ammono-Basic Lead Nitrate, $Pb_2N(NO_3).nNH_3$(?).—The basic compound formed as described above by the action of potassium amide upon a solution of lead nitrate is obtained as a white, or

slightly yellow, amorphous precipitate which does not settle well and which is therefore washed with considerable difficulty. Small portions of the dry product dropped upon water are vigorously decomposed; in the case of larger pieces the decomposition is sometimes accompanied by explosions. Heated in a glass tube the substance explodes. All that can be said at the present time concerning this product is that determinations of lead and ammonia in two poorly washed specimens show it to be an ammonobasic mixture. Analyses of two specimens gave, respectively, 79.0 and 79.8 per cent. lead, 7.6 and 7.2 per cent. nitrogen and 4.9 and 1.0 per cent. potassium nitrate, which had not been removed during the washing of the precipitate. The results of further work on this compound will be given in a later paper.

Bismuth Nitride, BiN.—When bismuth iodide is brought into contact with liquid ammonia it goes rapidly into solution, leaving behind a reddish brown residue, presumably of a basic salt, which is increased in amount by the addition of potassium amide to the solution. When bismuth iodide is run into a solution of potassium amide, a darker brown precipitate is formed, and there is deposited at the same time more or less metallic bismuth as a mirror on the walls of the containing tube. The precipitate settles well and is easily washed. When the precipitate is dried its color changes to very dark brown, almost black, and it seems always to undergo gradual decomposition as is indicated by the fact that metallic bismuth is always left behind on treating the dried precipitate with dilute hydrochloric acid preparatory to analysis. The dry substance explodes on being heated or on coming into contact with water or dilute acids. It is indeed so sensitive that four of the eight attempts to prepare the compound ended in inexplicable explosions. For analysis, the dry substance was decomposed by the slow action of water vapor, after which in the case of Specimen I it was dissolved in nitric acid, while Specimens II and III were treated with dilute hydrochloric acid. Complete solution accompanied by the evolution of red fumes followed the treatment of the first preparation with nitric acid. Residues of metallic bismuth remained undissolved after the action of dilute hydrochloric acid on the other two specimens.

Bismuth bromide also dissolves freely in liquid ammonia with the separation of a bulky, white mass of a basic salt which dissolves in excess of ammonium bromide. This solution gives the same

brown precipitate of bismuth nitride when added to a solution of potassium amide. Preparation III below was made from bismuth bromide.

I. 0.0986 gram of the substance, after solution in dilute HNO_3, gave 0.1070 gram Bi_2O_3 and 0.0037 gram N.

II. One-half of 0.2779 gram substance treated with dilute HCl gave 0.1380 gram Bi_2O_3 and 0.00821 gram N; the other half of 0.2779 gram of the substance gave 0.1377 gram Bi_2O_3 and 0.00821 gram N. The insoluble residue was lost. The ratio of Bi to N in the soluble portion is 1.015 to 1.000.

III. 0.2376 gram substance left on treatment with dilute HCl 0.0335 gram of residue and gave 0.2350 gram Bi_2S_3 and 0.0128 gram N.

	Calculated for BiN.	Found. I.	II.	III.
Bi	93.7	97.3	89.2	80.4
N	6.3	3.7	5.9	5.4
Residue	.....	0.0	lost	14.1

If the percentages of bismuth and nitrogen in the soluble portions only of Specimens II and III are calculated, then the following results are obtained:

	Calculated for BiN.	Found. I.	II.
Bi	93.7	93.7	93.6
N	6.3	6.2	6.3

These are in the best of agreement with the formula BiN. The product obtained, as described above, is therefore, a mixture of bismuth nitride and metallic bismuth. A similar reducing action of the potassium amide solution, the cause for which is not obvious, has been observed many times in connection with the experiments on the silver, lead, mercury and copper compounds.

Bismuth nitride has been prepared from both bismuth iodide and bismuth bromide in accordance with the equations

$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3$$

and

$$BiI_3 + 3KNH_2 = BiN + 3KI + 2NH_3.$$

Action of Potassium Amide on Aluminum Iodide.—Aluminum iodide reacts vigorously with ammonia gas, much heat is evolved, and, if the action is allowed to proceed rapidly, much ammonium iodide is volatilized and condensed on the cooler portions of the tube. On condensing ammonia upon the reaction-mixture everything goes into solution with the exception of a small quantity of a white residue which may be either an ammono-basic salt or possibly an impurity from the aluminum iodide used. When aluminum iodide is added to a potassium amide solution a white precipitate is formed, which dissolves immediately in excess of the latter solution. A permanent precipitate is formed when the aluminum iodide is in excess. This precipitate is white, very bulky, and refuses to settle well, so that complete washing by decantation is practically impossible. When the solution of the white precipitate in excess of potassium amide is evaporated, the solution becomes thick and viscous without showing any signs of crystallization, whence it appears that the prospects for the isolation of a potassium aluminum derivative of ammonia are not promising.

The results of the analyses of two separate preparations of the white basic precipitate gave respectively: for aluminum 20.7 and 21.6 per cent., for nitrogen 30.9 and 29.6 per cent., and for iodine 41.8 and 44.0 per cent., while a third specimen gave 23.6 per cent. nitrogen. These results lead to no very probable compound, but agree roughly with either of the formulas Al_2IN_5 and Al_2IN_6. The precipitate, therefore, may be an equimolecular mixture of aluminum amide, $Al(NH_2)_3$, and aluminum iodo-amide, $AlI(NH_2)_2$. It is in any case an ammono-basic product.

Action of Ammonia on Antimony Iodide.—Ammonia gas acts upon antimony iodide with the evolution of heat and the formation of a white addition product, which by the action of liquid ammonia is gradually converted into a pure yellow, pulverulent mass. The product is apparently insoluble in ammonia, or in a solution of either ammonium iodide or potassium amide.

The analysis of a specimen which was allowed to lie in contact with a solution of potassium amide over night gave 74.3 per cent antimony, and 9.6 per cent. nitrogen. Iodine was not determined quantitatively, but was proved to be present by a qualitative test. Analysis of the product of the action of ammonia

alone on antimony iodide gave as the results of two separate experiments, 70.8 and 73.4 per cent. antimony, 10.8 and 9.8 per cent. nitrogen and 15.1 and 15.7 per cent. iodine. Calculation from the mean of these results leads approximately to the formula Sb_5N_6I. This formula may be interpreted as the basic compound $(NH_2)_2SbI.4SbN$, or what is perhaps more probable, the reaction mass is simply a mixture of antimony nitride with unchanged antimony iodide. A mixture of one molecule of $SbI_3.4NH_3$ with 14 molecules of SbN would have a composition close to that of the products of the above experiments.

The impure antimony nitride as above prepared is pure yellow in color, and explodes, but with little violence, when heated or when dropped into water or dilute acids.

The antimony and aluminum derivatives of ammonia will receive further attention in this laboratory.

SUMMARY.

In this paper attention is called to the striking parallelism between the physical properties of the two electrolytic solvents, water and ammonia.

The close analogy between the relations of the acid amides, the metallic amides, and the metallic derivatives of the acid amides to ammonia on the one hand, and the relations of the ordinary oxygen acids, bases and salts to water on the other, is emphasized, and a system for naming the former class of derivatives is proposed.

The ammonia derivatives bearing to ammonia the relations which the ordinary salts, bases and acids bear to water are given the names, *ammono-salts*, *ammono-bases* and *ammono-acids*.

The word *ammonolysis* is offered as a suitable designation for a class of reactions in which ammonia plays a part analogous to the action of water in ordinary hydrolytic reactions.

The so-called mercuri-ammonium compounds of the literature are interpreted as belonging to one of three classes of ammonia derivatives: first, compounds related to ammonia as ordinary basic compounds are related to water; second, salts with ammonia of crystallization; and third, mixed compounds basic to both ammonia and water.

In the experimental part are given details of work from which the following general conclusions are drawn:

Salts of the heavy metals in solution in liquid ammonia react with the soluble amides of the alkali metals to form amides, imides or nitrides of the former in a manner analogous to the formation of insoluble hydroxides and oxides in aqueous solutions.

Certain metallic salts undergo ammonolysis in liquid ammonia in a manner analogous to hydrolytic decomposition in water.

Many metallic salts, when in excess, react with soluble metallic amides to give ammono-basic salts after the manner of the formation of ordinary basic salts in water solutions.

The insoluble metallic amides, imides, and nitrides, as well as the ammono-basic salts, dissolve in liquid ammonia solutions of ammonium salts in a manner analogous to the solution of the corresponding oxygen compounds in aqueous acids.

Certain ammono-bases dissolve in excess of potassium amide solution in a manner analogous to the solution of certain metallic hydroxides in aqueous potassium hydroxide.

The following compounds have been prepared from liquid ammonia solutions:

Silver amide, $AgNH_2$.
Mercuric nitride, Hg_3N_2.
Ammono-basic mercuric iodide, Hg_2NI.
Ammono-basic mercuric bromide, Hg_2NBr.
Ammono-basic mercuric chloride, $HgNH_2Cl$.
Lead imide, PbNH.
Ammono-basic lead iodide, $Pb_2NI.NH_3$.
Bismuth nitride, BiN.

STANFORD UNIVERSITY, CALIFORNIA,
April, 1905.

THE BOILING-POINTS OF AMMONIA, METHYL AMINE, METHYL CHLORIDE AND SULPHUR DIOXIDE.

BY H. D. GIBBS.

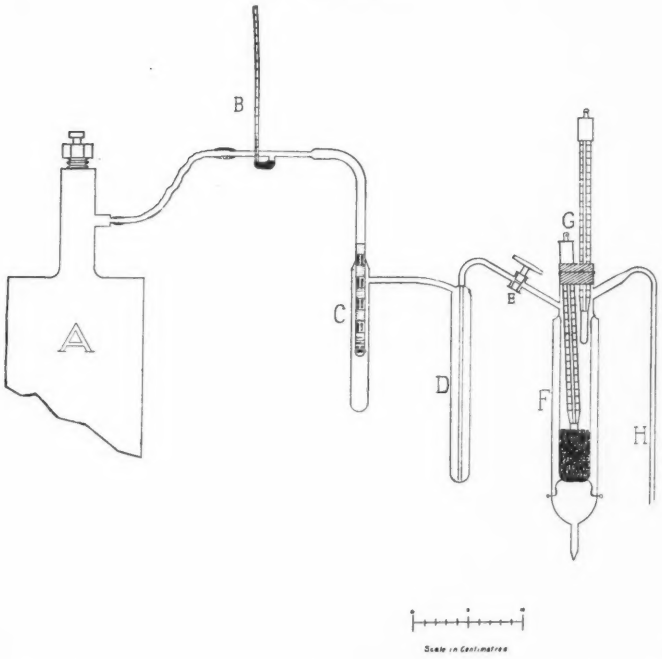
Received May 1, 1905.

THE VALUES given in the literature for the boiling-points of a number of low-boiling liquids have been determined almost exclusively by means of measurements of the vapor-pressures, and as there is a great lack of agreement in the various results, the writer has undertaken a criticism and revision of the earlier work and a direct determination of the boiling-points. Improved meth-

ods for purifying the liquids, thermometers which have been compared with the normal thermometer of the Reichsanstalt, and a specially designed apparatus have been employed for the determinations.

Work which is being carried on in this laboratory makes the determination of the boiling-points of ammonia and methyl amine desirable, and as the apparatus was applicable for the determination of the values for methyl chloride and sulphur dioxide, their boiling-points lying in the same neighborhood and their literature showing the same lack of agreement, the work was extended to include them also.

THE APPARATUS.



The liquids (ammonia, methyl amine, methyl chloride and sulphur dioxide) contained in steel or glass cylinders, *A*, are distilled into the tube *D*, and there condensed by a surrounding cooling-

mixture, either ice-water or liquid ammonia, contained in a Dewar test-tube. During the process of distillation the gases are freed from any dust or material dissolved in the liquid, which might be carried along mechanically, by the filter *C*. This filter is composed of layers of carefully prepared asbestos fiber, separated to avoid too close packing, by bundles of fine glass rods or tubes. The asbestos layers are, however, so dense that the gases penetrate slowly and condense slowly and regularly in the tube *D*. The gas pressure during the distillation is indicated by the manometer *B*. The efficiency of this device was shown by the discoloration of the upper layer of asbestos fiber. The discoloration rarely extended to the second layer.

During the operation of filling the receptacle *D* the stop-cock *E* must be closed to retain the liquid. This stop-cock was carefully ground and no difficulty was experienced in holding liquid ammonia when the pressure, as shown by the manometer, was in the neighborhood of eight atmospheres. The vessel *F*, in which the liquids are boiled for the purpose of measuring their temperatures of ebullition, consists of an inner and outer tube sealed together, the space between being exhausted of air to provide a vacuum jacket for the inner tube. On opening the stop-cock *E* the tube *D* is emptied of its liquid contents into the boling tube *F*. That portion of the liquid which is vaporized in cooling *F* and during the boiling passes out through the tube *H*, at which point it is condensed in order to prevent loss of the liquid and contamination of the atmosphere of the room by introducing the tube *H* into a glass cylinder which is cooled by liquid ammonia or carbon dioxide in ether, contained in a Dewar test-tube of suitable size.

The liquid is made to boil in *F* by passing an electric current from a 110-volt alternating circuit through the platinum wires sealed into the bottom of the tube through the vacuum jacket. The bubbles of the boiling liquid are broken up by a deep layer of garnets. Thermometers, *G*, pass through a cork or rubber stopper which closes the inner tube tightly. All joints in the apparatus are made by sealing the glass tubes together, except where the steel cylinder is connected to the glass, at which point small lead tubing is used joined to the glass by sealing-wax.

During the boiling of the liquid the tube *F* is surrounded by a large empty Dewar test-tube to further provide against changes of temperature by absorption of heat from the outside. No diffi-

culty is experienced in reading the thermometers through the four thicknesses of glass. A rather long focus lens is employed for this purpose.

The capacity of the inner tube of *F* is 8 cc. to cover the garnets, 66 cc. to the top of the vacuum-jacketed portion and 75 cc. to the opening of the outlet tube. With the thermometer in place the corresponding capacities are 8 cc., 61 cc. and 68 cc.

THE THERMOMETERS.

Four different thermometers were used in the various determinations: No. 21713 is a toluene thermometer graduated in fifths of a degree from —20° to —50° in a space of 10 cm. The total length of the thermometer is 20 cm. According to the certificate of the Reichsanstalt it requires no correction.

Number 21714 is a duplicate of the former, but according to the Reichsanstalt certificate accompanying it the readings of the thermometer at

$$\left.\begin{matrix}-25^\circ\\-35^\circ\\-45^\circ\end{matrix}\right\} \text{are} \left\{\begin{matrix}0.1\\0.4\\0.3\end{matrix}\right\} \text{degree too high.}$$

These thermometers are calibrated to the nearest tenth of a degree.

Number 3972 is a mercury thermometer graduated in half-degrees from —8° to +100° in a space of 25 cm. The total length of the thermometer is 34 cm. According to the accompanying certificate of the Reichsanstalt it requires no correction below 25° to the nearest tenth of a degree.

The fourth thermometer has not been standardized by the Reichsanstalt, but was corrected by careful comparison with the three above mentioned. It is a mercury thermometer, graduated in half-degrees from —42° to +54° in a space of 22 cm. The total length of the thermometer is 31 cm.

It was found to require the following corrections:

$$\left.\begin{matrix}-\ 6.3^\circ\\-24.2^\circ\\-33.6^\circ\end{matrix}\right\} \left\{\begin{matrix}0.4\\0.0\\0.0\end{matrix}\right\} \text{too high.}$$

AMMONIA.

Review of the Literature.—Guyton[1] (1799) obtained liquid ammonia from a gas which he found to condense at a temperature of

[1] *Ann. de Chim.*, **29**, 290.

—48.75°. His method of purification was very imperfect and an accurate determination of the boiling-point was not made.

R. Bunsen,[1] in 1839, from his determinations of the vapor-pressures of liquid ammonia at varying temperatures, calculates the boiling-point to be —33.7°, the barometer corrected to 0° and 749.3 mm. pressure. It is evident that he had very pure ammonia for reasons which will be mentioned later.

Michael Faraday's[2] (1844) determinations of the vapor-pressures at temperatures ranging from 0° to 85° F. place the boiling-point near —40° C. at one atmosphere pressure.

A. Loir and Ch. Drion,[3] in 1860, found that the temperature of liquid ammonia at ebullition at atmospheric pressure is —35.7°.

Regnault,[4] in 1860, and two years later with improved apparatus, determined the vapor-pressures at varying temperatures and from these measurements calculated the boiling-point to be —32.6° at 760 mm. pressure. To check this result a determination was also made with an alcohol thermometer immersed in ammonia contained in an open vessel, and as a result of this experiment the boiling-point is stated as —38.5° at 752 mm. pressure.

Raoul Pictet,[5] in 1885, determined the vapor-pressures of liquid ammonia between —30° and 50°.

He states that the boiling-point is very low, namely —33°.

Blümke,[6] in 1888, also made a parallel series of determinations.

M. W. Travers[7] (1901), in commenting upon the determinations of Pictet and Blümke, says that the results of Pictet when plotted by the method of Ramsay and Young[8] give a fairly straight line.

"The smoothed results place the boiling-point at 760 mm. at 236° absolute (—37° C.). The results obtained by Blümke appear to be less reliable."

On the next page Travers gives the boiling-point of liquid ammonia as 234.5° absolute (—38.5° C.).

A. Joannis[9] (1892), in his investigations of the properties of

[1] *Pogg. Ann.*, **46**, 97 (1839).

[2] *Ann. chim. phys.* [3], **15**, 257 (1845); *Phil. Trans.*, **135**, 155 (1845).

[3] *Bull. Soc. Chim.* [Paris], 1860, p. 184.

[4] *Compt. Rend.*, **50**, 1072; *Jahresb.*, 1860, p. 40; *Ibid.*, 1863, p. 66; *Mem. de l'acad. des Sc. Inst. d. France*, **26**, 535 (1862).

[5] Nouvelles machines frigorique Genève, 1885: Arch. de Geneve, 1887; *Wied. Beibl.*, **11**, 629 (1887); *Arch. de Sc. Phys. et Nat.* [3], **13**, 212 (1885).

[6] *Wied. Ann.*, **34**, 10, 1888; *Jahresb.*, 1888, p. 152.

[7] "Study of Gases," p. 246.

[8] *Phil. Mag.*, **21**, 33 (1886).

[9] *Compt. Rend.*, **115**, 820 (1892).

some liquid ammonia solutions, states that the boiling-point is —38.2° at 764 mm. pressure.

Other statements concerning the boiling-point which cannot be traced to their sources are Dickerson,[1] —33°; Lange,[2] —33.7°, probably a copy of Bunsen's figures, and —33.5°.[3]

The statements in all of the text-books and larger work on chemistry, concerning the boiling-point of liquid ammonia, vary from the figures obtained by Bunsen, —33.7° at 749.3 mm., to those of Faraday, —40° at one atmosphere.

Criticisms of Some of the Earlier Methods and Results.—The vapor-pressure method for the determination of the boiling-points of liquids requires carefully purified material if results at all accurate are to be obtained. The presence of very small quantities of air, or other constituents which are more volatile than the liquid, greatly increases the vapor-pressure, while non-volatile impurities produce an opposite, but far less conspicuous effect. The high vapor-pressures, and consequently low boiling-points, as determined by Faraday, Pictet and Blümke are accounted for if one is permitted to assume the presence of air or other gases in their ammonia. From these considerations it appears that Bunsen had a very pure sample of ammonia.

Observations have shown that liquid ammonia exposed to the air in an open vessel is almost certain to cool below the boiling-point, even if vigorously stirred, the supercooling readily going far enough to solidify mercury. The low results of Regnault are thus accounted for.

Purification of the Ammonia.—Sodium dissolves in liquid ammonia to form the well-known blue solution. On long standing, or quickly under the influence of platinum sponge or ferric oxide[4] there is generated from this blue solution, hydrogen and sodamide according to the equation

$$NH_3 + Na = NaNH_2 + H.$$

Any moisture which may be in the liquid ammonia is converted by the sodium into hydrogen and sodium hydroxide or by the sodium amide into ammonia and sodium hydroxide. The latter reaction is represented by the equation

$$NaNH_2 + H_2O = NaOH + NH_3.$$

[1] "Liquid Air," by T. O'Connor Sloane, Ed., London, 1900.
[2] "Verflüsigtes Ammoniak als Lösungsmittel," by J. Bronn, p. 9.
[3] "Chemiker-Kalendar," 1905, p. 17.
[4] Franklin, This Journal, **27**, 820.

These reactions are made use of in drying the liquid ammonia.

Into a steel cylinder of about two liters capacity, a quantity of freshly cut sodium is placed, the screw caps are put in place and commercial liquid ammonia is siphoned in. The cylinder stood in this condition for several weeks before using. It is connected to the glass portion of the apparatus by means of small lead tubing and sealing-wax, as shown in the figure, and the ammonia is then ready to be distilled out of the steel cylinder through the filter *C* and condensed in the receptacle *D*.

The Boiling-Point Determination.—The toluene thermometers (Nos. 21713 and 21714) were put in place through a rubber stopper which was found to be practically not affected by the ammonia. First one thermometer was passed as far as possible through one hole in the stopper and into the garnets, the other thermometer being inserted only far enough to close the other hole. During the boiling of the liquid the positions of the thermometers were interchanged. Liquid ammonia was run into *F* until the inner tube was filled to the outlet tube which placed the entire toluene thread of the thermometer in the liquid. The current from an alternating incandescent circuit was passed through the platinum spiral, the regulating being done by means of lamp resistance.

The resistance of the spiral is 1.1 ohms. The energy consumed in boiling the liquid was from 18 to 40 watts. The higher energy expenditure boiled the liquid violently.

The thermometer was placed in position in the liquid and allowed to stand sometimes as long as an hour, then the current was turned on and the boiling continued until the thermometer became constant, which usually required only four or five minutes. Readings of the barometer and thermometer were then taken at intervals of about three minutes until it was evident that there was no variation. In some cases the boiling was continued for twenty-five minutes. The loss of liquid during this time was from 25 per cent. to 50 per cent. of the total, depending upon the rate of ebullition.

The relative positions of the thermometers were then changed and more liquid passed in to make up the loss by evaporation and the determination repeated.

The apparatus was then disconnected from the steel cylinder, the garnets removed and thoroughly cleaned, the tube *F* thoroughly cleaned and dried, the thermometers put in place and dry

air drawn through the entire apparatus for at least three hours when the apparatus was ready for the next determination.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	14.1	759.2	757.4[1]	21713	−33.60[2]	0.0	−33.60	−33.53
				21714	−33.25[3]	−0.35	−33.60	−33.53
				4	−33.55[4]	0.0	−33.55	−33.48
II.	16.8	757.9	755.7	21713	−33.44[5]	0.0	−33.44	−33.32
				21714	−33.20[6]	−0.34	−33.54	−33.42
				4	−33.60[7]	0.0	−33.60	−33.48
							Mean,	−33.46

No correction was necessary for capillarity in the form of barometer employed.

The observed boiling-points at the observed barometric pressures (corrected to 0.0°) are calculated to 760 mm. pressure by means of the formula $\frac{dP}{Pd\overline{T}} = \frac{Q^*}{2\overline{T}^2}$, in which P is the pressure in gram-centimeter units, T the absolute temperature and Q the molecular heat of volatilization of the liquid expressed in small calories. In the case in question dP and $d\overline{T}$ can be taken as the direct differences in pressure and temperature without introducing an appreciable error. By means of these calculations, we are enabled to compare the various results and determine the mean value. The heat of volatilization of liquid ammonia is taken as 330[9] small calories per gram.

Criticisms of the Results.—In the direct determination of the boiling-point of a liquid boiling below the temperature of the laboratory, the vapor must invariably become superheated, with

[1] Ostwald-Luther: "Physiko-Chemische Messungen," 2nd Ed., p. 121.
[2] Constant for 18 minutes.
[3] During 8 minutes changed 0.02°.
[4] During 11 minutes changed 0.05°.
[5] During 9 minutes changed 0.04°.
[6] Constant for 7 minutes.
[7] During 7 minutes changed 0.05°.
[8] "Vorlesungen über Theoretische und Physikalische Chemie," by J. H. van't Hoff, Vol. I. p. 13 (1900).
[9] Franklin and Kraus: *Am. Chem. J.*, **21**, 8 (1899).

the result that a too high boiling-point is indicated if the thermometer is placed in the escaping vapor. Vigorous boiling and bright metallic protecting screens together with the vacuum jacket would minimize but probably not entirely eliminate this source of error. Hence the immersion of the thermometer in the liquid was resorted to. This method is, generally speaking, objectionable because of the superheating of the liquid, but this is avoided by the platinum wires sealed into the bottom of the tube and the garnets, the apparatus in this form being employed by Beckmann[1] for exact boiling-point determinations.

Another possible objection to this method is that the thermometer should show a higher reading when the bulb is deeply immersed in the liquid than when only slightly immersed (neglecting the exposed thread of the thermometer liquid), for the lower layers of the liquid are under greater pressure than the upper layers. Increase of pressure not only raises the boiling-point of the lower layers of the liquids but will also have an effect on the glass of the thermometer bulb. This latter is probably negligible and no variation could be noticed with the thermometers employed as the liquid boiled away, reducing the height of its column.

A more probable source of error when the toluene thermometers were employed, was the slowness of the running down and settling to place of the toluene. Every precaution was taken to avoid the introduction of error from this cause.

METHYL AMINE.

Review of the Literature.—E. D'Andreeff[2] (1859) states that the boiling-point of methyl amine is observed to be below 0° and calculated to be —8°.

A. W. Hofmann[3] (1889) determined the boiling-point of liquid methyl amine, employing for the purpose the apparatus described by Bannow,[4] which consisted of a flask of platinum foil 0.5 mm. thick, divided into two hemispheres 7.5 cm. in diameter and made tight at the flanged point of union with packing. In the throat of the upper hemisphere is a cork carrying a glass tube 1 cm. by 15 cm. which is surrounded by a glass mantle through which cold water could be run during the determination. The thermom-

[1] *Z. physik. Chem.*, **4**, 593 : **8**, 223 : **15**, 661 ; **18**, 492 : **21**, 245 ; **40**, 129 (1902).
[2] *Ann. chim. phys.* (3), **56**, 332.
[3] *Ber. chem. Ges.*, **22**, 699 (1889).
[4] "Die Chemische Industrie," 1886, p. 328.

eter passed through the inner tube a short distance below the cork and was for its whole length in the vapor of the boiling liquid. It was compared with the normal thermometer of the Reichsanstalt.

For each determination 100 cc. of the methyl amine were distilled over sodium: Barometer, 768.35; air temperature, 4.0°; duration of investigation, twenty-five minutes; boiling-point, —6.0° to —5.5°.

Criticisms.—It is evident that Hofmann's results are influenced by the fact that the temperature of the methyl amine vapor, in which the thermometer stood, is raised by the surrounding atmosphere, the temperature of which is stated to be 4.0°, that is, 10.0° above the boiling-point given for the liquid. Too high a value for the boiling-point would thus be expected.

Purification of the Methyl Amine.—Liquid methyl amine behaves toward metallic sodium in a manner analogous to that of liquid ammonia. The reaction producing the methyl sodamide,

$$CH_3.NH_2 + Na = CH_3.NHNa + H,$$

progresses much more slowly than the corresponding ammonia reaction[1].

Ten grams of freshly cut metallic sodium were placed in a steel cylinder of about 500 cc. capacity and methyl amine distilled in from a number of glass cylinders in which it was stored in the liquid condition. This methyl amine was a portion of a kilo purchased from Kahlbaum through the kindness of the trustees of the Bache Fund to whom acknowledgments are due. The steel cylinder was connected to the glass portion of the apparatus in the same manner as described under ammonia.

The Boiling-Point Determination.—The apparatus employed was identical with that used for the ammonia determination except that a different thermometer was used, and, as rubber is very quickly acted upon by methyl amine, the thermometers were supported by a cork stopper which closed the opening to the inner tube of *F*.

Thermometers number 3972 and 4 were used and the entire mercury threads of both thermometers were in the boiling liquid throughout each determination.

The same care was used in cleaning and drying the apparatus

[1] Franklin and Kraus: *Am. Chem. J.*, **24**, 83 (1900).

before each determination as in the liquid ammonia determinations, and the boiling was conducted in the same manner.

The methyl amine vaporizing from the apparatus was carefully collected, in a tube cooled by liquid ammonia, for use in other investigations of its properties.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.
I.	13.6°	757.6	755.8	3972	—6.7[1]	0.0	—6.7
				4	—6.3[2]	—0.4	—6.7
II.	16.0°	757.6	755.5	3972	—6.7[3]	0.0	—6.7
				4	—6.3[4]	—0.4	—6.7
						Mean,	—6.7

The heat of volatilization of methyl amine not being known, the results cannot be reduced to standard conditions by the method employed for liquid ammonia.

METHYL CHLORIDE.

Review of the Literature.—Regnault[5] (1863), from determinations of the vapor-pressure, calculates the boiling-point to be——23.73° at 760 mm. pressure. .

Berthelot[6] states the boiling-point as —21°.

Camille Vincent[7] (1877) obtained a colorless, mobile liquid, which boiled at —23° at 760 mm. pressure, by distillation of trimethyl amine hydrochloride.

Camille Vincent and Dalachanal[8] (1879) state, in their determination of the densities of methyl chloride, that the boiling-point is —23.7°.

Travers[9] says the boiling-point is —24°, but no authority is given for the statement.

[1] Constant for 4 minutes.
[2] Constant for 4 minutes.
[3] Constant for 19 minutes while liquid was three-fourths boiled away.
[4] Constant for 15 minutes.
[5] *Jahresb.*, 1863, p. 70.
[6] Beilstein, 3rd Ed., Vol. **1**, p. 144.
[7] *Compt. Rend.*, **85**, 667; *Jahresb.*, 1877, p. 398.
[8] *Ann. chim. phys.* [5], **16**, 427; *Bull. Soc. Chim.*, **31**, 11.
[9] "Study of Gases," p. 54.

Purification of the Methyl Chloride.—The methyl chloride was prepared by the method of Groves[1] by passing dry hydrochloric acid into methyl alcohol, which contained dissolved zinc chloride. The methyl chloride was passed through a tower of potassium hydroxide in sticks, then through concentrated sulphuric acid and then condensed in glass cylinders cooled by a surrounding mixture of solid carbon dioxide dissolved in ether. It was thus partially, if not wholly, freed of hydrochloric acid and moisture.

From these cylinders, the methyl chloride was distilled and condensed in the receptacle *D*, the gas first passing through a purifying chain consisting of two tubes 25 cm. in length filled with soda-lime, two tubes of the same size containing phosphorus pentoxide, and the asbestos filter *C* with manometer which have been previously described.

The distillation of the methyl chloride through the purifying apparatus to the condensing tube *D* is carried on slowly so as to insure complete purification; in fact, the phosphorus pentoxide tubes and the filter *C* were packed so tightly that the distillation could not progress rapidly.

The Boiling-Point Determination.—Thermometers 21713, 21714 and 4 were employed and the determination was carried out in exactly the same manner as described under ammonia.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	16.85	760.2	758.0	21713	—24.05[2]	0.0	—24.05	—23.98
				21714	—24.1[3]	—0.1	—24.20	—24.13
				4	—24.2[4]	0.0	—24.2	—24.13
II.	18.1	760.5	758.1	21713	—24.15[5]	0.0	—24.15	—24.09
				21714	—24.10[6]	—0.1	—24.20	—24.14
				4	—24.1[7]	0.0	—24.1	—24.04
							Mean,	—24.09

[1] *J. Chem. Soc.*, 1874, p. 641; *Ann. Chem.* (Liebig), **174**, 378.
[2] During 5 minutes varied 0.05°.
[3] During 4 minutes varied 0.05°.
[4] Constant for 6 minutes.
[5] During 6 minutes varied 0.05°.
[6] Constant for 4 minutes.
[7] Constant for 8 minutes.

The heat of volatilization of methyl chloride is taken as 96.9[1] small calories per gram.

SULPHUR DIOXIDE.

Review of the Literature.—R. Bunsen[2] (1839), by determinations of the vapor-pressures at several different temperatures, places the boiling-point at —10.5°; barometer, 744 mm. corrected to 0°.

Michael Faraday[3] (1845), by measurements of the vapor-pressure, finds the boiling-point to be —10° at one atmosphere pressure.

Pierre[4] (1847) determined the boiling-point as —8° at 759.18 mm. pressure.

Ch. Drion[5] (1859) states the boiling-point to be —8°.

E. D. Andreeff[6] (1859) gives the boiling-point as —10.3° at 741 mm.; —9.9° at 754 mm.

Regnault[7] (1860) gives the vapor-pressure as 762.49 mm. at —10°, and later, in 1863,[8] by measurements of the vapor-pressures, he determined the boiling-point to be —10°.08 at 760 mm. pressure.

Pierre[9] (1873), by boiling the liquid in 25- or 30-gram portions, found the boiling-point to be —8°.

R. Pictet[10] (1877) found the boiling-point to be —10° at one atmosphere pressure by the vapor-pressure method.

A. Blümcke[11] (1888), by determinations of the vapor-pressure, finds the boiling-point to be —10° at 1.01 atmospheres pressure.

Purification of the Sulphur Dioxide.—The commercial sample of the sulphur dioxide was distilled from a steel cylinder through two phosphorus pentoxide tubes, each 25 cm. long, through the filter *C*, and condensed in the tube *D*. The distillation was carried on slowly, the tube *D* being cooled by liquid ammonia.

The Boiling-Point Determination.—Thermometer number 4 was the only one available for this determination which was otherwise carried out as previously described for the other liquids.

[1] Chappius: *Ann. chim. phys.* [6], **15,** 517 (1888).
[2] Pogg. *Ann.*, **46,** 97 (1839).
[3] *Ann. chim. phys.* [3], **15,** 257 (1845); *Phil. Trans.*, **135,** 155 (1845).
[4] *Ann. chim. phys.* [3], **21,** 336; *Jahresb.*, 1847, p. 63.
[5] *Ann. chim. phys.* [3], **56,** 5; *Jahresb.*, 1859, p. 18.
[6] *Ann. Chim. Pharm.*, **110,** 1; *Ann. chim phys* [3], **56,** 317; *Jahresb.*, 1859, p. 19
[7] *Compt. Rend.*, **50,** 1072 (1860); *Jahresb.*, 1860, p. 41.
[8] *Ann. chim. phys.* [3], **15,** 134; *Jahresb.*, 1863, p. 70.
[9] *Compt. Rend.*, **76,** 214.
[10] *Ann. Phys. and Chem. Beibl.* (Wiedemann), 1887, **11,** 629; *Arch. de Sc. Phys. Nat.* [3], **13,** 212 (1885).
[11] *Wied. Ann.*, **34,** 10 (1888); *Jahresb.*, 1888, p. 152.

The boiling was carried on for one hour and six minutes, the liquid almost boiling away in this time, the variation in temperature during this time being 0.13°, namely, —9.60 to —9.73°.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	19.1	763.4	760.90	4	—9.73[1]	—0.33	—10.06	—10.09

The value for the heat of volatilization of sulphur dioxide is taken as 91.7[2] small calories per gram.

These results are open to the same criticisms as those for ammonia, and in addition it is to be regretted that the objection may also be made that the thermometer was not compared with the normal thermometer of the Reichsanstalt.

SUMMARY.

(1) The literature of the boiling-points of ammonia, methyl amine, methyl chloride, and sulphur dioxide, has been collected and the various results criticized.

(2) The boiling-points of these liquids have been redetermined, improved apparatus, method of working and means for purifying the liquids, having been employed.

(3) As a result of the work the boiling-point of ammonia is found to be —33.46° at 760 mm.

(4) The boiling-point of methyl amine is found to be —6.7° at 755.67 mm. No value for the heat of volatilization of the liquid is available for calculating the value at 760 mm.

(5) The boiling-point of methyl chloride is found to be —24.09° at 760 mm.

(6) The boiling-point of sulphur dioxide is found to be —10.09 at 760 mm.

This work was undertaken at the suggestion of Professor E. C. Franklin, of Stanford University, carried to completion under his

[1] During 34 minutes the boiling-point changed 0.01° and the liquid almost completely boiled away.

[2] Chappius: *Ann. chim. phys.* [6], **15**, 513; *Compt. Rend.*, **104**, 897 (1897).

kindly advice and assistance, and I wish to express my grateful thanks to him and acknowledge the many favors shown me.

STANFORD UNIVERSITY,
January 31, 1905.

Note.—The methods employed for the purification of the ammonia used in these experiments precludes the possibility of the presence of objectionable quantities of impurities other than possibly pyridine and its homologues. Tests for pyridine, by the method of H. Ost[1] failed to show more than traces of that substance in the liquid, which was not so highly purified as that used for the boiling-point determinations.

Franklin and Kraus[2] have shown the boiling-point elevation constant of ammonia to be 3.4, a value smaller than that of any other known liquid, whence it follows that nearly 3 per cent. of pyridine by weight must be present to produce a change in the boiling-point of the solvent of 0.1 degree. Since tests have shown that nothing approaching such a quantity was present, the conclusion is justified that the value given in this paper for the boiling-point of liquid ammonia can not be appreciably in error from the presence of impurities in the ammonia used.

I am indebted to Dr. William A. Noyes for the suggestion that tests for pyridine be made.

H. D. GIBBS.

FOOD LABORATORY,
SAN FRANCISCO, CALIFORNIA,
June 12, 1905.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 58. SENT BY H. W. WILEY.]

CHEMICAL GLASSWARE.

BY PERCY H. WALKER.

Received April 28, 1905.

It is unnecessary to call the attention of the analytical chemist to the fact that all glass is more or less soluble in water and in various solutions. He simply accepts the fact and when working with the greatest care avoids, as far as possible, the use of glass. Of really greater practical importance than the difference in solu-

[1] "Commercial Organic Analysis," Allen, Vol. III, Part II, p. 104.

[2] *Amer. Chem. J.*, **20**, 846 (1898).

bility of different kinds of glass is the difference they show as regards breaking and cracking by changes of temperature. One may make some allowance for the fact that the glass is partly dissolved in the course of analysis, for with many single determinations it makes no practical difference, but the patience of the analyst is sorely tried when an important determination is ruined by a beaker cracking on heating on a water-bath or hot plate.

In order to make a comparison of different kinds of chemical glassware the following samples were secured:

No. 2009. Flasks, of Kavalier Bohemian glass.

No. 2010. Beakers same as 2009. Kavalier's glass bears no trade mark.

No. 2011. Flasks of Weber's resistance glass, also known as Greiner and Friedrichs' resistance glass. Trade mark R.

No. 2012. Beakers same as 2011.

No. 2013. Flasks of Wiener Normal glass. Trade mark, "Wiener Normal Geräthe Glas."

No. 2014. Beakers same as 2013.

No. 2019. Beakers, Thüringen glass. No distinctive mark.

No. 2020. Beakers, flasks and Erlenmeyer flasks, Jena glass. Trade mark "Schott and Gen. Jena."

No. 2021. Beakers of "Nonsol" glass. Trade mark "Nonsol W. T. Co."

No. 2022. Beakers, flasks and Erlenmeyer flasks. Laboratory glassware, American. Makers' name on pasted label, but no permanent mark.

No. 2023. Beakers, Bohemian Normal glass from an American dealer. Paper label, but no permanent mark.

No. 2041. Beakers. Resistance glass of Vereinigte Fabriken für Laboratoriumsbedarf. No distinguishing mark.

No. 2042. Flasks. Same as No. 2041.

No. 2043. Beakers. F. Z. resistance glass. Trade mark "FZ."

No. 2044. Flasks same as No. 2043.

No. 2057. Bohemian glass beakers from an American dealer.

While it is well known that no great amount of information can be had from an analysis of glass, analyses were made of beakers of all the different kinds of glass. In most cases this analysis was simply a silicate analysis, using well-known methods. The precautions necessary have been very thoroughly discussed by Hillebrand.[1]

[1] Bulletin No. 176 of the United States Geological Survey.

The determination of boron presents some difficulty. The most satisfactory method is the combination of Gooch and Thomson methods used by Sargent in the determination of boron in tourmaline.[1] The use of mannite in the titration is to be preferred to glycerol, which Sargent used.

TESTS APPLIED.

A. Preliminary Treatment.—All samples before testing are carefully washed with pure water, filled with pure water and allowed to stand at a temperature of 20° to 25° C. for twenty-four hours, then rinsed with pure water and dried.

B. Mechanical Tests.—(1) (Applies only to beakers.) Fill beaker one-quarter full with a 10 per cent. solution of common salt, place on steam table and evaporate to complete dryness. Dissolve residue in water and repeat evaporation. This process is repeated four times, the beaker being finally left on steam table for six hours after it has become dry. After each evaporation careful examination is made for minute cracks.

(2) (When possible, use a beaker or flask of from 400 to 600 cc. capacity.) Fill half-full with water at 20 ° C. Place on a platinum triangle and heat with the direct flame of a Bunsen burner. The flame should be 12 cm. high, and top of burner 8 cm. below the bottom of the beaker.

(3) Pour boiling water into the beaker or flask at 20° C.

(4) Boil water in beaker or flask, empty and plunge into water at 20° C.

C. Solubility Tests.—(5) Carefully dry and weigh the vessel. Add 100 cc. of a 2 per cent. solution of sodium carbonate, cover and heat to boiling on a hot plate and boil twenty minutes, empty, wash with water, hydrochloric acid and again with water, dry and weigh. In testing beakers, but not flasks, the sodium carbonate solution is returned to the beaker and evaporated uncovered on the steam table to dryness, washed as before and weighed.

(6) Same as (5) except that a 2 per cent. solution of potassium hydroxide is used instead of the sodium carbonate.

(7) Same as (5), except that a 4 per cent. solution of ammonium carbonate is used.

(8) Place 100 cc. of neutral water in the vessels, cover with platinum dishes and keep on steam table for forty-eight hours, cool

[1] This Journal, **21**, 858.

and again make up to 150 cc. with neutral water, and take 100 cc. of this for titration. Place this 100 cc. in a stoppered bottle and add 20 cc. of an ethereal solution of iodoeosin (0.002 gram to 1000 cc.). On shaking, if any alkali is in the water it turns pink and this color is discharged by adding dilute acid. A N/50 sulphuric acid is used.[1]

(9) Fill vessels with the purest water that can be obtained, allow to stand at a temperature of 20° to 25° C. for twenty-four hours and determine the electrical conductivity. The conductivity measurements were made by Dr. Buckingham of the Bureau of Soils.

Of these tests the first is the only one that is new; it was suggested by Mr. L. S. Munson who had used it for several years before this work was taken up.

Table I shows the results of analyses of the different kinds of glass. As was to be expected, no very great amount of information can be gotten from this table, but it is of interest to note that we may divide the glasses into two distinct groups, Nos. 2010, 2019, 2022, 2023, 2041 and 2057 being alkali lime silicates, while Nos. 2012, 2014, 2020, 2021 and 2043 are borosilicates that have part of the lime replaced by zinc. It is also of interest that all of the borosilicate glasses may be distinguished by a permanent trade mark, and that these are the only glasses, so far as the writer has been able to learn, that are so distinguished.

Table II shows the results of the tests applied. Nos. 2020, 2021, 2012, 2043, 2014 and 2010 stood test No. 1. No. 2022 failed on the fourth evaporation in this test, No. 2041 on the third evaporation, and Nos. 2019, 2023 and 2057 failed on the first evaporation. It is interesting to note that of the six samples that stood this test five were the five trade-marked borosilicate glasses, the sixth sample being Kavalier's Bohemian glass.

Nos. 2020, 2021, 2012, 2043, 2014 and 2010 stood test No. 2. No. 2041 failed badly, and occasional samples of Nos. 2019, 2022, 2023 and 2057, failed. This test is not as useful as test No. 1. Where a very large number of samples are handled it is found that even with the most resistant glass occasional pieces will fail, while the greater number will stand; but with test No. 1 we have not ob-

[1] Mylius and Foerster: "Ueber die Bestimmung kleiner Mengen von Alkali und die Erkennung der Neutralitat des Wassers." *Ber.*, **24**, 1482.

TABLE I.—ANALYSES OF GLASSES EXAMINED.

Serial No.	SiO_2.	B_2O_3.	As_2O_5.	$(AlFe)_2O_3$.	ZnO.	MnO.	CaO.	MgO.	K_2O	Na_2O.	$M'_2O:M''O:\left\{\frac{B_2O_3}{SiO_2}\right\}$
2010	76.02			0.64		Trace	7.38	0.30	7.72	7.60	1.49 : 1 : 9.04
2012	68.00	5.53	0.24	2.32	2.40	0.14	4.80	5.04	1.82	10.17	0.75 : 1 : 5.01
2014	74.00	2.15		0.66	0.24	0.01	7.76	0.16	5.51	9.69	1.48 : 1 : 8.71
2019	74.36			0.90		Trace	9.40	0.16	0.14	14.83	1.41 : 1 : 7.24
2020	66.74	7.88		2.77	8.28	0.65	0.28	4.50	0.08	8.99	0.56 : 1 : 4.73
2021	65.04	6.23		3.78	8.88	0.04	1.75	1.44	0.08	12.72	1.15 : 1 : 6.55
2022	68.09			2.08		1.12	5.90	3.82	6.49	12.32	1.24 : 1 : 5.25
2023	73.80			1.00		1.04	7.88	0.08	7.67	8.59	1.38 : 1 : 7.38
2041	77.48			0.66		Trace	4.86	0.20	7.52	9.14	2.43 : 1 : 13.79
2043	68.96	6.02		0.70	8.65	0.11	0.26	5.05	3.64	6.71	0.62 : 1 : 5.25
2057	71.44			2.00		1.12	8.10	0.89	2.73	13.91	1.40 : 1 : 6.54

TABLE II.—RESULTS OF TESTS APPLIED.

Serial No.		Test 1.	Test 2.	Test 3.	Test 4.	Test 5. Loss in milligrams. A.	Test 5. Loss in milligrams. B.	Test 6. Loss in milligrams. A.	Test 6. Loss in milligrams. B.	Test 7. Loss in milligrams. A.	Test 7. Loss in milligrams. B.	Test 8. cc. N/50 H_2SO_4.	Test 9.
2009	Flask	.....	Good	Good	Good	11.0	....	7.8	....	0.8	...	0.85	300
2010	Beaker	Good	Good	Good	Good	11.2	20.4	12.2	18.6	0.8	1.8	0.20	298
2011	Flask	.....	Good	Good	Good	8.4	....	8.6	....	0.0	...	0.35	291
2012	Beaker	Good	Good	Good	Good	5.5	6.7	9.2	17.0	0.0	1.2	0.18	288
2013	Flask	.....	Good	Good	Good	15.0	....	8.8	....	1.4	...	0.90	299
2014	Beaker	Good	Good	Good	Good	11.8	20.9	18.3	24.7	1.4	3.6	0.20	295
2019	Beaker	Bad	Fair	Good	Good	7.0	22.2	10.8	17.0	1.0	2.6	0.09	295
2020	Beaker	Good	Good	Good	Good	3.8	4.4	16.4	26.4	1.2	2.4	0.10	294
2020	Flask	Good	Good	Good	Good	4.6	....	....	....	...	...	0.24	...
2021	Beaker	Good	Good	Good	Good	4.8	6.0	17.8	23.4	0.8	2.0	0.23	296
2022	Beaker	Bad	Fair	Good	Good	12.2	24.2	15.6	22.8	0.6	3.2	0.63	298
2022	Flask	.....	.....	.....	.....	72.0	....	....	....	...	...	5.08	...
2023	Beaker	Bad	Fair	Good	Good	12.4	24.0	10.2	16.6	0.6	1.8	0.22	337
2041	Beaker	Bad	Bad	Good	Good	10.0	21.0	9.17	17.0	1.9	1.9	0.65	...
2042	Flask	.....	Good	Good	Good	14.2	....	5.4	....	0.8	...	3.07	...
2043	Beaker	Good	Good	Good	Good	5.4	5.6	9.6	16.5	2.6	3.3	0.00	...
2044	Flask	.....	Good	Good	Good	8.2	....	6.6	....	2.8	...	0.39	...
2057	Beaker	Bad	Fair	Good	Good	....	....	....	....	...	...	0.17	...

served that any samples of the best glasses fail, and nearly all of the poorer grades fail in the first four evaporations.

Nothing can be learned from tests Nos. 3 and 4, as all the samples examined stood these tests.

In examining the results of the solubility tests one observes that there is in some cases a great difference between the solubilities of beakers and flasks of the same kind of glass, and as we had beakers of each kind and flasks of only a part of the samples, it is better in comparing the different kinds of glass to confine our attention for the present to the results on the beakers. In tests Nos. 5, 6 and 7 the columns marked A give the losses in milligrams after boiling with the solvent for twenty minutes, and columns marked B give the total losses after evaporating to dryness on the water-bath. Owing to the different shapes of beakers and consequent unequal evaporation and unequal changes in concentration, the losses on boiling for twenty minutes are much more variable than those by evaporating to dryness on the steam table. If we examine the results of test No. 5, column B, we see that we can divide the samples into two groups differing very much in solubility; the least soluble group Nos. 2020, 2043, 2021 and 2012 are all borosilicate glasses containing considerable zinc. Of the more soluble group No. 2014 is the only zinc borosilicate, and this glass contains much less zinc and boric acid than the other trade-mark glasses.

In test No. 6 we do not find the marked difference in solubility that was shown in test No. 5. Three of the borosilicate glasses, Nos. 2021, 2014 and 2020, are the most soluble, but the other two, Nos. 2043 and 2012, are among the least soluble. This test agrees with the results of Glinzer,[1] and of other observers who have pointed out that Jena glass is less soluble in carbonated alkalies and more soluble in hydrated alkalies than Bohemian glass. One would expect that the other borosilicate glasses would show the same peculiarity, but Nos. 2043 and 2012 seem to be remarkable in being slightly attacked by both carbonated and hydrated alkali.

Test No. 7 shows very little except that fixed alkalies have more effect on glass than ammonia. The amounts dissolved are in all cases so small that comparisons between the different samples are of very little value.

Test No. 8 is an important one, and while it cannot be taken

[1] *Z. angew. Chem.*, 1894, p. 743.

alone as a means of judging a glass, if taken in connection with test No. 1, can give one an excellent idea of the relative merits of different glasses. If we consider simply the beakers here, we see that all of those that required more than 0.4 cc. N/50 sulphuric acid were proved to be very poor glass by the other tests.

Test No. 9 was disappointing, an inspection of the results showing little difference between good and bad glass. The figures given are merely comparative, as the capacity of the cell used was not determined. The water used had a specific conductivity of 6.5×10^{-6} at 19°. While it is possible that somewhat better results may be gotten by using purer water, there appears to be no advantage in using this test, since test No. 8 gives us the necessary information as to solubility in water.

An examination of the results on flasks and a comparison of the results on the corresponding beakers shows the rather peculiar fact that a glass in the form of beakers seems to be more resistant to reagents than the same glass in the form of flasks. The writer cannot attempt to explain this peculiarity, but it is probably due to some difference in the annealing of the different forms of apparatus.

Some tests were made on the action of acids on glass, but the results only confirmed the conclusions of other investigators that glasses at all suitable for chemical work are much less attacked by acids than by alkalies or even water alone, consequently the tests with acid were soon abandoned.

One of the most prolific writers on the testing of chemical glassware has been Foerster, and it may be instructive to note in Table III the results of one of his investigations. This table is compiled from tables given in Foerster's article entitled "Vergleichende Prüfung einiger Glassosten hinsichtlich ihres Chemischen Verhaltens."[1] This table, among other things, shows that while the amount of alkali dissolved in hot water does not show the total matter dissolved by the water, yet it does show that alkali gives a very fair means of judging the relative solubility of the glass, and as in good glass the total matter dissolved is very small, its determination by loss of weight would be far from exact. Unfortunately, we can not take Foerster's determinations, which were published over eleven years ago, as necessarily bearing on glasses on the market at this time. Nos. 1, 2 and 10 are Jena glass, but a comparison of these analyses with those given in Table

[1] *Z. anal. Chem.*, **33**, 381.

TABLE III.—ANALYSES AND TESTS FROM FOERSTER'S WORK.

Number of glass.	K_2O.	Na_2O.	CaO.	ZnO.	MnO.	$(AlFe)_2O_3$.	SiO_2.	B_2O_3.	$R'_2O:R''O:SiO_2$	Number of alkali molecules in 100 molecules.	Alkali given up to water expressed in thousandths of a milligram of Na_2O.	
											In eight days at 20°.	In three hours at 80°.
1....	....	11.0	....	....	0.05	5.0	71.95	12.0	....	10.8	2.5	2.7
2....	....	9.8	7.0	5.0	0.3	3.5	74.4	....	0.84 : 1 : 6.59	10.0	2.1	6.3
3....	5.8	7.6	10.4	....	....	0.3	75.9	....	0.99 : 1 : 6.81	11.2	10.7	28.4
4....	6.6	6.7	9.5	....	....	0.6	76.6	....	1.05 : 1 : 7.52	11.0	8.9	28.2
5....	6.2	6.4	10.0	....	0 2	0.4	76.8	....	0.95 : 1 : 7.16	10.4	13.1	26.8
6....	7.0	8.3	8.1	....	....	0.3	76.3	....	1.44 : 1 : 8.80	12.7	14.0	56.0
7....	11.8	4.9	7.6	....	0.1	0.5	75.1	....	1.50 : 1 : 9.24	12.8	14.5	45.0
8....	4.3	10.0	7.8	....	....	0.3	77.6	....	1.48 : 1 : 9.28	12.6	14.9	50.0
9....	4.6	10.1	7.7	....	....	0.4	77.2	....	1.54 : 1 : 9.36	13.0	17.8	66.0
10....	....	14.0	7.0	7.0	....	2.5	67.5	2.0	1.06 : 1 : 5.41	14.0	16.6	65.0
11....	0.6	14.3	11.2	....	0.4	2.9	70.6	....	1.18 : 1 : 5.88	14.6	27.0	98.0
12....	14.0	1.0	5.8	....	0.1	0.2	78.9	....	1.59 : 1 : 12.7	10.4	....	....
13....	1.8	12.9	11.0	....	....	1.3	73.0	....	1.16 : 1 : 6.20	13.8	....	....
14....	....	....	....	....	....	...	....	....	....	....	....	....
15....	9.7	9.0	6.8	....	Trace	0.4	74.1	....	2.04 : 1 : 10.17	15.4	32.0	217.0
16....	6.7	13.7	7.2	.... PbO	0.3	3.2	68.9	....	2.27 : 1 : 8.91	18.6	77.0	654.0
17....	12.7	....	....	30.0	....	...	57.3	....	1.00 : 1 : 7.10	11.0	74.0	350.0

TABLE III.—ANALYSES AND TESTS FROM FOERSTER'S WORK (*Continued*).

Number of glass.	Ratio of alkali given up to cold and hot water.	Loss in weight on three hours' treatment at 100° with 2 N alkali expressed in milligrams.		By treatment at 190° for four hours with water was dissolved in milligrams.			Number of molecules of silicic acid dissolved in water at 190° to each molecule of alkali dissolved.	Description of samples.
		Sodium hydrate.	Sodium carbonate.	Total.	Alkali.	Na_2O corresponding to the dissolved alkali.		
1....	1.1	67.3	23.5	23.7	3.5	3.5	6.0	Lime-free sodium borosilicate.
2....	3.0	39.7	17.6	....	....	....	....	Zinc lime glass containing aluminum, poor in sodium.
3....	2.65	35.4	....	....	....	....	....	Glass rich in lime, poor in alkali.
4....	3.17	37.5	59.5	17.2	5.6	4.6	2.65	Glass rich in lime, poor in alkali.
5....	2.05	....	....	....	....	....	....	Glass rich in lime, poor in alkali.
6....	4.00	39.8	76.9	....	....	....	....	Good lime alkali glass.
7....	3.10	37.7	79.2	51.3	15.4	11.1	3.35	Good lime alkali glass.
8....	3.40	38.5	73.0	....	....	....	....	Good lime alkali glass.
9....	3.72	42.4	79.4	67.0	16.4	14.7	3.57	Good lime alkali glass.
10....	3.91	46.5	23.0	34.0	6.4	6.4	4.42	Lime soda glass containing zinc oxide and aluminum.
11....	3.63	31.3	40.7	?	7.3	7.3	....	Lime-rich soda glass containing aluminum.
12....	....	....	....	63.0	16.2	10.7	4.5	Good potash glass, poor in lime.
13....	....	....	....	37.0	8.3	8.3	3.6	Lime-rich soda glass.
14....	....	....	....	87.0	....	29.0	....	
15....	6.78	....	....	....	....	....	....	Alkali-rich glass.
16....	8.5	46.0	45.0	126.0	61.0	52.0	1.3	Alkali-rich glass containing aluminum.
17....	4.73	58.0	51.0	....	....	....	....	Lead crystal glass.

I shows that none of them are the same as the Jena glass on the American market.

Nos. 3, 4 and 5 of Table III are said to be the glasses used by Stas. It is seen that these are good glasses and they approach the "normal" formula, the ratio $R_2O : R^{II}O : SiO_2$ approaching that of 1 : 1 : 6.

That this "normal" formula of a glass does not give us any guarantee that the glass is of good quality is shown by an inspection of the analyses and tests of samples Nos. 2010, 2022 and 2057. Nos. 2022 and 2057 have a ratio approaching much more nearly the normal ratio than No. 2010, and yet these two glasses are very poor glasses and No. 2010 is a good one.

In general, the conclusion to be drawn from this investigation is that the trade-mark glasses are zinc borosilicate glasses. That of these the Wiener Normal glass is the least resistant to reagents and the properties more nearly resemble the alkali lime silicate glasses. That of the other trade-mark glasses there is so very little difference in quality that the choice may be reduced to a simple consideration of price. That the alkali lime silicate glasses found on the American market are usually of very poor quality. This inferior quality is very probably due to the fact that the consumer has no means of identifying the different makes. He may order Kavalier's glass and may be furnished glass that was made by an entirely different factory. One thing that we need is that all makers of chemical glassware mark their products with some distinct and permanent trade mark, and when that is done we can learn which trade marks mean good glass and know that we are getting what we order. This has been done by the makers of the borosilicate glass, but there is undoubtedly a demand for good glass of the Bohemian type.

The writer, in conclusion, wishes to express his obligations to Mr. L. S. Munson for many suggestions in connection with this work.

CONTRACTS LABORATORY, BUREAU OF CHEMISTRY,
WASHINGTON, D. C., April 14, 1905.

[Contributions from the Chemical Laboratory of Harvard College.]

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

SECOND PAPER

By Gregory Paul Baxter.

Received May 15, 1905.

Very recently, in an investigation upon the atomic weight of iodine,[1] the value 126.975 for this constant was obtained as the average from three closely agreeing ratios. Experiments subsequent to the publication of this research have shown that the results of all three methods were subject to slight errors, and that the atomic weight of iodine is even slightly higher than the above value. Following is a description of these experiments, with details where the processes differed from those previously described. For further information the first paper should be consulted.

THE RATIO OF SILVER IODIDE TO SILVER BROMIDE AND SILVER CHLORIDE.

In the previous investigation the ratio AgI : AgCl was determined by heating silver iodide in a current of chlorine in six experiments which yielded an average result of 126.975, calculated upon the basis of silver 107.93 and chlorine 35.467. The latter value for chlorine was a preliminary one, found in an investigation by Richards and Wells then in progress in this laboratory. Later experiments by these chemists have shown that the atomic weight of chlorine is in reality 35.473,[2] which necessitates a positive correction for the atomic weight of iodine of 0.010. The corrected value, 126.985, agrees very closely with two determinations, made in the course of the earlier investigation, in which silver iodide was heated in a current of carbon dioxide and bromine. Assuming the atomic weight of bromine to be 79.955, the value found by Stas and repeatedly verified by experimenters in this laboratory,[3] these two determinations give the values 126.987 and 126.985. The results obtained by reference both to chlorine and to bromine thus became almost identical. However, in order to confirm these two determinations with bromine, further experi-

[1] Baxter: *Proc. Am. Acad. of Arts and Sci.*, **40**, 419 (1904); also *Z. anorg. Chem.*, **43**, 14; This Journal, **26**, 1577.

[2] Richards and Wells: "Publications of the Carnegie Institution, No. 28 (1905); also This Journal, **27**, 459.

[3] Richards: *Proc. Amer. Phil. Soc.*, **43**, 119

ments were carried out in the same manner as before, as follows:

Pure silver iodide was prepared as described in the previous paper, by precipitating pure silver nitrate with a considerable excess of the purest ammonium iodide,[1] washing the precipitate with 1 per cent. nitric acid and pure water, and drying the iodide, in an air-bath, and then by fusion in a tared quartz crucible, first in an atmosphere containing free iodine, and finally in air to expel dissolved iodine. Fusion in an atmosphere containing iodine must have completely converted occluded silver nitrate into silver iodide. The iodide was then heated in a current of air and bromine. The air was purified by being conducted successively over beads moistened with silver nitrate solution, sodium carbonate, and finally concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. Four different samples of bromine were employed, each one of which had been thrice distilled from a solution of a bromide, in each distillation the bromide having been made from a portion of the product of the previous distillation. Chlorine must have been completely separated in this way. The presence of iodine in the bromine was of less importance. Nevertheless each sample, while in the form of hydrobromic acid, was freed from iodine by boiling with several small portions of potassium permanganate. The apparatus for purifying the air and saturating the air with bromine was so constructed that the gases came in contact only with glass. The quartz crucibles were always contained in large porcelain crucibles during the heating in bromine, as well as in the initial fusion of the silver iodide with iodine. Volatilization of the silver halides was prevented by heating very gently at first, at a temperature insufficient to fuse the mixture, then, when the greater part of the iodine had been replaced, until the silver bromide barely fused. Furthermore, the crucible was very deep and the current of gases very slow, so that any volatilized silver halides had opportunity to condense upon the cool walls of the crucible. That no loss from volatilization actually took place was certain for two reasons. In the first place, the weight of the bromide in most cases became constant within a few hundredths of a milligram after once being heated, although subsequently the salt was maintained at a temperature slightly above its melting-point,

[1] The method of purifying the iodine is described briefly on page 879 of this paper.

for at least an hour. In the second place, the perforated cover and hard glass delivery tube for the bromine, when rinsed with ammonia and the solution treated with hydrochloric acid in excess, gave no visible trace of opalescence. Before the salt was allowed to solidify it was maintained above its fusing-point in air for a few minutes to eliminate dissolved bromine.

The silver bromide resulting from each analysis was converted into silver chloride by heating in a current of pure dry chlorine in a similar fashion.[1] Here also constant weight within a very few hundredths of a milligram was easily obtained, and as before the perforated cover and inlet tube were free from weighable amounts of chloride. It has already been shown that silver chloride and silver iodide when fused in an atmosphere of the corresponding halogens and then in air, retain none of the halogen.[2] The quartz crucibles remained almost absolutely constant in weight during these experiments. From the ratio between the original silver iodide and the silver chloride the atomic weight of iodine was calculated.

The following vacuum corrections were applied: silver iodide, +0.000071; silver bromide, +0.000046; silver chloride, +0.000075.[3] The analyses of Series II were obtained through the bromide, those of Series III are the results from the previous paper recalculated from the higher atomic weight of chlorine, with the exception of Analysis 18, which was made subsequently. All completed analyses are recorded in the tables. Several were lost, owing to breaking of the crucibles.

TABLE I.

Series I. AgI : AgBr.

Number of analysis.	Sample of bromine.	Weight of silver iodide in vacuum. Grams.	Weight of silver bromide in vacuum. Grams.	Atomic weight of iodine.
1	A	13.65457	10.92091	126.985
2	A	17.35528	13.88062	126.987
3	B	9.70100	7.75896	126.982
4	B	10.27105	8.21484	126.983
5	B	9.85688	7.88351	126.986
6	C	8.62870	6.90106	126.991
7	D	11.92405	9.53704	126.981
8	D	7.56933	6.05389	126.987
			Average,	126.985

[1] For preparation and purification of chlorine, see earlier paper.

[2] See previous paper; also Richards and Wells: *Loc. cit.*, p. 59, and Köthner and Aeuer: *Ann. Chem.* (Liebig), **337**, 127.

[3] The value for the specific gravity of silver chloride is assumed to be 5.56, as determined by Richards and Stull in this laboratory. In the previous paper this value was incorrectly taken as 5.62.

Series II. AgI : AgCl.

Number of analysis.	Weight of silver iodide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
9	13.65457	8.33538	126.985
10	17.35528	10.59457	126.983
11	10.27105	6.27006	126.980
12	8.62870	5.26735	126.985
13	11.92405	7.27926	126.976
		Average,	126.982

Series III. AgI : AgCl.

Number of analysis.	Weight of silver iodide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
14	9.26860	5.65787	126.990
15	6.72061	4.10259	126.984
16	11.31825	6.90912	126.987
17	10.07029	6.14754	126.979
18	13.49229	8.23649	126.980
		Average,	126.984

THE RATIOS BETWEEN SILVER, IODINE, AND SILVER IODIDE.

In the earlier paper determinations of the ratios of silver to silver iodide and iodine were described. It remained to determine the ratio of iodine to silver iodide. For this purpose iodine was purified as before by thrice converting it into hydriodic acid with hydrogen sulphide, and then heating the hydriodic acid with a slight excess of potassium permanganate which had been freed from chlorine by crystallization. The final product of iodine was distilled once with steam, freed from water by suction upon a porcelain Gooch crucible, and dried as far as possible in a desiccator over concentrated sulphuric acid. It was then sublimed once from porcelain boats in a current of pure, dry air in a hard glass tube, and then a second time from the hard glass tube into the weighing-tube, which was constructed as described in the first paper. This weighing-tube remained constant in weight within a few hundredths of a milligram in each experiment, and lost in weight in all only 0.1 mg. in the eight final analyses. Next, the iodine was dissolved in sulphurous acid, and was then precipitated by adding a solution of a slight excess of pure silver to the solution of hydriodic acid in a precipitating flask. The silver iodide clotted together very rapidly in the presence of the nitric acid and excess of silver, and offered none of the difficulties met when the precipitation is carried out with an excess of iodide, for

it may be washed indefinitely with pure cold water without showing the least tendency to pass into colloidal solution. The silver iodide was collected upon a Gooch crucible, dried and weighed. The loss on fusion was determined, and the asbestos shreds in the filtrate were collected. Twelve determinations carried out in this way with solutions varying from tenth- to thirtieth-normal gave results from 126.93 to 126.98. The variations were finally traced to the carrying-down of silver nitrate by the silver iodide, for the more concentrated the solutions during the precipitation and the greater the excess of silver employed, the lower was the observed atomic weight of iodine. The occlusion of silver nitrate by silver halides is well known in the cases of silver bromide and silver chloride, but in these cases it is possible to wash out the occluded salts by oft-repeated treatment with water. The difficulty in removing the silver nitrate in the case of silver iodide is doubtless due to the lesser solubility of this halide. Similar observations have been made by Köthner and Aeuer,[1] who found that with fifth-normal solutions the carrying-down of silver nitrate is very considerable, and that an excess of iodide converts this occluded silver nitrate into silver iodide only very slowly if at all. They found, however, that, if the precipitated silver iodide is washed with ammonia, the greater part of the occluded matter may be eliminated, owing possibly to the slight solubility of silver iodide in ammonia. On account of this newly discovered tendency of silver iodide, it seemed probable that the results of the synthesis of silver iodide from known weights of silver in the early part of this research were somewhat too low, for although the precipitations took place in ammoniacal solution and an excess of iodine was employed, the fact that the solutions were always very nearly as strong as tenth-normal and that the ammonium iodide was poured into the silver nitrate made it probable that occlusion had taken place at least to some extent even here. It is noteworthy that three of these syntheses yielded results as high as 126.985. Similar conclusions are to be drawn concerning the results of the titration of silver and iodine, although in this case precipitation took place in the reverse fashion, *i. e.*, by adding the silver nitrate to the iodide.

Accordingly, experiments were carried out for the redetermination of the ratios of silver to silver iodide and to iodine, as well as the new one of iodine to silver iodide, with special precautions to

[1] *Ann. Chem.* (Liebig), **337**, 123.

avoid the error of occlusion by using very dilute solutions and no excess of silver. After the iodine had been weighed, very nearly the exact amount of silver to combine with the iodine was weighed out and dissolved in nitric acid with the usual precautions to avoid spattering. The quantity of iodine used in each analysis was between 3 and 4 grams, and the amount of silver consequently about 3 grams. The solutions of both silver and iodine were diluted to a volume of 1 liter each, so that the solutions were about thirtieth-normal, and then the silver nitrate was added very slowly to the solution of hydriodic acid with constant stirring. The flask in which precipitation was carried out was then shaken for some time, and allowed to stand until the supernatant liquid was clear. This liquid was tested for an excess of iodine or silver in a nephelometer,[1] and if a deficiency of either was found it was made up and the solution again shaken, until the point was reached where the extremely faint opalescence produced by both hydriodic acid and silver nitrate was equal in both nephelometer tubes. The excess or deficiency of silver was in no case over 0.1 mg., and in most cases much less.

Several samples of iodine were employed in these analyses, each one of which had been distilled three times from an iodide as previously described. Three different specimens of silver, purified by different methods, were used. Sample A was a portion of the material used in the first investigation. Sample B was prepared from silver nitrate which had been recrystallized seven times from nitric acid, five times from water, and finally precipitated by ammonium formiate.[2] Sample C was precipitated as silver chloride once, electrolyzed once, and finally precipitated with formic acid. All three samples were fused in a current of hydrogen on a lime boat. In order to determine whether an even more gradual addition of silver nitrate would influence the extent of the occlusion, in Analysis 23 the silver was introduced by means of a large funnel provided with a fine spout.

The vacuum corrections, —0.000031 for silver and +0.000102 for iodine were applied. The atomic weight of silver is assumed to be 107.930, as before.

[1] Richards and Wells: *Am. Chem. J.*, **31**, 235.

[2] Richards and Wells: Publications of the Carnegie Institution, No. 28, p. 19.

TABLE II.

Series IV. Ag : I.

Number of analysis.	Sample of silver.	Weight of iodine in vacuum. Grams.	Weight of silver in vacuum. Grams.	Atomic weight of iodine.
19	A	3.29308	2.79897	126.983
20	B	3.70132	3.14584	126.988
21	B	3.75641	3.19258	126.991
22	B	3.24954	2.76186	126.988
23	A	4.12541	3.50639	126.984
24	C	3.53166	3.00165	126.988
25	C	2.99835	2.54842	126.985
26	C	2.00015	1.69991	126.993
			Average,	126.987

In one of the foregoing analyses the attempt was made to determine the ratio between iodine and silver iodide by adding an excess of silver nitrate and weighing the precipitate. Although only 5 mg. excess of silver nitrate were added, and the total volume of the liquid was over 2 liters, the precipitate was 1 mg. heavier than it should have been as calculated from the result of the titration, showing that the occlusion of silver nitrate by the silver iodide may take place even after precipitation. In order to avoid this difficulty, in succeeding analyses the silver iodide was collected without the addition of silver nitrate, after washing with pure water; then the dissolved silver iodide was determined in the filtrate and wash-water, by comparing the precipitates produced by the addition of silver nitrate with those formed in standard solutions of hydriodic acid. As a matter of fact, the filtrates were always found to be practically free from silver iodide, while the wash-waters contained from 0.2 to 0.4 mg. per liter. This difference in solubility of the silver iodide in the filtrate and wash-waters is probably due to colloidal solubility of this salt in pure water. The loss on fusion of the silver iodide and the asbestos shreds were determined as usual. The almost absolute lack of opalescence in the filtrate when treated with silver nitrate or hydriodic acid is a good proof of the complete absence of chlorine and bromine, since both silver bromide and silver chloride are considerably more soluble than the iodide.

TABLE III.

Series V. I : AgI.

Number of analysis.	Weight of iodine in vacuum. Grams.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
27	3.75641	6.94913	126.987
28	3.24954	6.01137	126.989
29	4.12541	7.63204	126.977
30	3.53166	6.53351	126.979
31	2.99835	5.54682	126.983
		Average,	126.983

Finally, in order to determine the ratio of silver to silver iodide, the filtrate and wash-waters were evaporated to very small bulk, until the greater part of the nitric acid had been expelled, and then the amount of silver in the residue was determined nephelometrically, after dilution to 25 cc., by adding an excess of hydriodic acid and comparing with standard solutions of silver. This quantity, which was never more than 0.1 mg., was subtracted from the original weight of silver, and no correction was applied to the weight of silver iodide for the amount dissolved in the wash-water.

TABLE IV.

Series VI. Ag : AgI.

Number of analysis.	Sample of silver.	Corrected weight of silver in vacuum. Grams.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
32	B	3.19249	6.94877	126.990
33	B	2.76175	6.01110	126.986
34	C	3.00189	6.53399	126.993
35	C	2.54833	5.54659	126.986
			Average,	126.989

The close agreement of the averages of the different series makes it certain that no constant error of magnitude still remained undetected in any one of the methods.

In Series I, II and III, the three chief possible errors have been considered and shown to have no effect. Occluded silver nitrate in the silver iodide was eliminated by fusion in iodine, and it was proved both that no volatilization of the halides actually took place and that no halogen was retained by the solidified salt. In Series IV, V and VI, the chief possible error, that of occlusion of silver nitrate by silver iodide, was avoided by sufficiently diluting the solutions before precipitation. That the dilution was sufficient was evident from the agreement of the results of the experi-

ments with the larger and smaller quantities of material, the total volume of the solutions being the same in all cases. Furthermore, the weight of the silver iodide obtained in the analyses recorded in Series V was in every case very nearly equal to the sum of the weights of silver and iodine employed (Series IV), which could not have been the case if silver nitrate had been retained by the iodide. One is forced, then, to conclude that the average of all six series, 126.985, represents the atomic weight of iodine within a very few thousandths of a unit, and that the results of the syntheses of silver iodide described in the first paper are slightly too low, owing to occlusion of silver nitrate by the silver iodide. Furthermore, the agreement of the results from silver bromide with those of the other series is an indication that the assumed atomic weight of bromine, 79.955, is very nearly correct. However, from the weights of silver bromide and silver chloride produced in the same analyses, the atomic weight of bromine may be computed.

TABLE V.

Series VII. AgBr : AgCl.

Sample of bromine.	Weight of silver bromide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of bromine.
A	10.92091	8.33538	79.955
A	13.88062	10.59457	79.951
B	8.21484	6.27006	79.952
B	7.87887	6.01352	79.956
C	6.90106	5.26735	79.951
D	9.53704	7.27926	79.952
		Average,	79.953

Stas's value and the value obtained in this laboratory[1] are thus confirmed. A repetition of these experiments with precipitated fused silver bromide is now under way.

Shortly after the publication of my first paper upon the atomic weight of iodine there appeared the complete paper of Köthner and Aeuer upon the same subject.[2] These chemists, by determining the ratio AgI : AgCl, obtained the value 126.936 (Cl = 35.45; Ag = 107.93) as the average of eight closely agreeing analyses. One synthesis, by precipitating a weighed amount of silver with hydriodic acid, gave the value 126.978, and from one synthesis by

[1] Richards: *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **337**, 123 (1904).

heating a weighed amount of silver in iodine the result 126.963 was obtained. A second paper[1] by the same authors contains a recalculation of their results from the higher value of chlorine, 35.467, and a critical discussion of their own, Ladenburg's[2] and my work. In this second paper two main criticisms of my investigation are made. One of these concerns the validity of the conclusion that ordinary iodine does not contain an undiscovered halogen element. This criticism is founded upon a mistaken understanding, however. My experiments were directed to prove the existence or non-existence of an element of *higher* atomic weight than iodine, which, if its properties were those to be expected from the properties of the other members of the halogen family, would have been set free from solutions of its compounds by iodine, and hence would have accumulated in the first fraction of the fractional separation (see page 1580 of the first paper). The existence of an unknown halogen of lower atomic weight than iodine was not considered.

Although Köthner assumes the possibility that such an element exists, it is obviously improbable that any halogen of lower atomic weight could have remained in the purified samples of iodine which were employed in my experiments; since those specimens which received even the least purification were thrice distilled from an iodide, the iodide having been made in each distillation from nearly one-half the iodine from the previous distillation.

In the second place, it is maintained that volatilization of silver halides takes place when silver iodide is heated in a current of chlorine. This is undoubtedly true, unless precautions are taken to prevent the volatilization. Silver iodide is much more volatile at its fusing temperature than silver chloride; and if the original silver iodide is fused before the current of chlorine or bromide is begun, a loss may take place by volatilization or possibly by *spattering*. In my own work, however, fusion of the salt was always avoided until the greater part of the change had taken place. Proof that no volatilization of silver halides actually occurred in my experiments has already been given (page 877). It may be added that the close agreement of the results of Series I and II is additional evidence in the same direction; for any loss of silver bromide, which is the most volatile of the three halides, would

[1] *Ann. Chem.* (Liebig), **337**, 362 (1904).
[2] *Ber. chem. Ges.*, **35**, 2275.

have tended to raise the results of Series II above those of Series I, whereas such slight difference as exists is in the opposite direction.

Köthner's average result in the series AgI : AgCl, when recalculated upon the basis of chlorine 35.473, becomes 126.974. The slight difference between this value and the final result of the research described in this paper may be explained in several possible ways. A perusal of Köthner's paper does not make clear whether or not fusion of the silver iodide took place at the beginning of his experiments, so that it is uncertain whether the gain in weight of the coil of glass tubing, which was attached to the reaction tube, was due to volatilized silver halides or to attacking of the glass by the hot halogens. At any rate, it is hard to believe that a meter and a half of glass tubing subjected to the long-continued action of mixed chlorine and iodine at 150° should not have altered its weight somewhat. Furthermore, Köthner himself showed that the tube in which the reaction took place was slightly attacked by the fused silver chloride, but the nature of the correction for this attacking of the glass is uncertain. Finally, although the precaution was taken of fusing the silver iodide before the initial weighing, so that the salt must have been free from moisture, it was not fused in an atmosphere of iodine. Hence it is possible that the iodide still contained traces of occluded silver nitrate (or metallic silver). This deficiency in iodine, as well as the possible gain in weight of the apparatus during the experiment, would have lowered the atomic weight of iodine.

As far as Köthner's syntheses of silver iodide from weighed amounts of silver are concerned, it need only be said that, even assuming that occlusion was avoided in the synthesis in the wet way, and that in the synthesis in the dry way a single precipitation of the iodine from solution in an iodide had completely removed such impurities as chlorine and bromine, which would have accumulated in the silver iodide during the experiment, the fact that Richards and Wells[1] have shown that silver fused in the air or with borax and saltpeter, according to Stas, must contain oxygen, makes it certain that the results of Köthner's syntheses are too low.

I am indebted to the Cyrus M. Warren Fund for Research in Harvard University for platinum vessels, quartz crucibles and balance.

[1] Publications of the Carnegie Institution, No. 28, p. 62.

SUMMARY.

The results of this investigation are, then, as follows:

(1) The atomic weight of iodine is found to be 126.985 (Ag = 107.930), one one-hundredth of a unit higher than the value previously obtained. If silver is assumed to be 107.920 and oxygen 16.000, iodine becomes 126.973.

(2) The observation of Köthner and Aeuer that under certain conditions silver iodide occludes silver nitrate, and that this occluded salt cannot be removed by washing with water, is confirmed.

(3) Richards and Wells's value for the atomic weight of chlorine, 35.473, is substantiated.

(4) Stas's value for the atomic weight of bromine, 79.955, is shown to be very nearly correct.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
CAMBRIDGE, MASS., March 16, 1905.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE OPTICAL PROPERTIES OF CASTOR OIL, COD-LIVER OIL, NEAT'S-FOOT OIL, AND A FEW ESSENTIAL OILS.

BY HERMANN C. LYTHGOE.

Received May 8, 1905.

I. CASTOR OIL.

Castor oil is "a fixed oil expressed from the seeds of *Ricinus communis*. A pale yellowish or almost colorless, transparent, viscid liquid, having a faint, mild odor, and a bland, afterwards slightly acrid, and generally offensive taste; Sp. gr., 0.950 to 0.970 at 15° C.," U. S. Pharmacopoeia.

Several authorities state that castor oil rotates the plane of polarized light, although Allen claims that all the samples examined by him were inactive[1]. Deering and Redwood report that twenty-three samples of Indian castor oil, polarized in a 200 mm. tube in a Laurent instrument, gave readings from +7.6° to +9.7°[1]. This corresponds to from 21.9° to 28.0° Ventzke.

During the routine examination of drugs in this laboratory, there has been occasion to examine a large number of samples of

[1] Lewkowitsch: "Oils, Fats and Waxes," p. 420.

castor oil, most of which have been found to be pure. It is from these pure samples that the refraction table has been calculated. This table gives the readings of castor oil on the scale of the Zeiss butyro-refractometer for each half degree from 15° to 35° C., together with the corresponding values of n_D.

TABLE I.—REFRACTION OF CASTOR OIL.

Temp. °C.	Butyro-refractometer reading.	n_D.	Temp. °C.	Butyro-refractometer reading.	n_D.
35.0	72.0	1.4736	25.0	78.1	1.4773
34.5	72.3	1.4738	24.5	78.4	1.4775
34.0	72.6	1.4740	24.0	78.7	1.4776
33.5	72.9	1.4742	23.5	79.0	1.4778
33.0	73.2	1.4744	23.0	79.3	1.4780
32.5	73.5	1.4745	22.5	79.6	1.4782
32.0	73.8	1.4747	22.0	79.9	1.4784
31.5	74.1	1.4749	21.5	80.2	1.4785
31.0	74.4	1.4751	21.0	80.6	1.4787
30.5	74.7	1.4753	20.5	80.9	1.4789
30.0	75.0	1.4755	20.0	81.2	1.4791
29.5	75.3	1.4756	19.5	81.5	1.4793
29.0	75.6	1.4758	19.0	81.8	1.4795
28.5	75.9	1.4760	18.5	82.1	1.4797
28.0	76.2	1.4762	18.0	82.5	1.4798
27.5	76.5	1.4764	17.5	82.8	1.4800
27.0	76.9	1.4766	17.0	83.2	1.4802
26.5	77.2	1.4768	16.5	83.5	1.4804
26.0	77.5	1.4769	16.0	83.9	1.4806
25.5	77.8	1.4771	15.5	84.2	1.4808
25.0	78.1	1.4773	15.0	84.5	1.4809

In refracting castor oil with the butyro-refractometer, ordinary light can be employed, as but little color is given to the critical line. Owing to the extreme viscosity of the oil, a little longer time than usual must elapse before reading, in order that the sample may attain the temperature of the prisms. The prisms can easily be cleaned by the use of chloroform, as castor oil is isoluble in the petroleum ether usually employed for this purpose.

Table II gives a résumé of the analyses of the oils examined. It will be observed that the variations from the readings of the refraction table are very slight, and that the polarizations are within the limits of those of Deering and Redwood recorded above.

TABLE II.

	Variation from refraction figures, butyro scale.	Sp. gr. 15° C.	Polarization ° Ventzke, 200 mm. 20° C.
Number of samples...	44	15	15
Highest.....	±0.5	0.9622	+26.1
Lowest.....	0.0	0.9590	+23.4
Average.....	±0.25	0.9609	+24.1

Table III gives the constants of a sample of castor oil containing about 50 per cent. cottonseed oil, sold in Massachusetts[1], together with those of pure castor and cottonseed oils. The spurious nature of this sample was first pointed out by the refractometer and subsequently confirmed by other tests.

TABLE III.

	Castor oil.	Adulterated oil.	Cottonseed oil.
Butyro-refractometer reading at 20°...	81.2	75.0	70.9
Polarization, ° Ventzke.....	24.1	10.5	— 0.4
Specific gravity at 15°.....	0.961	0.9378	0.923
Iodine number (Hanus).....	85.0	99.4	109.0
Halphen test.....	....	Red	Red

II. COD-LIVER OIL.

Cod-liver oil "is a fixed oil obtained from the fresh livers of *Gadus Morrhua* and of other species of *Gadus*. A pale yellow, thin, oily liquid, having a peculiar, slightly fishy, but not rancid odor, and a bland, slightly fishy taste; sp. gr., 0.920 to 0.925 at 15° C.," U. S. Pharmacopoeia.

It is difficult to read cod-liver oil on the butyro-refractometer owing to the dispersion, the colored band extending over five scale divisions. This difficulty can be overcome by the use of sodium light, or easier, by a ray screen consisting of a parallel-sided bottle about 1.5 inches in diameter, containing a 10 per cent. solution of potassium bichromate, through which the light is allowed to pass before striking the mirror. There is, of course, no such difficulty when using the Abbé refractometer.

There is much more variation in the refraction of cod-liver oil than in the case of castor oil. Of about twenty samples the maximum variation from the butyro-refractometer readings of Table IV is ±1.3, and the average variation is ±0.6. Even with this marked variation it is easy to pick out a sample of oil to which a foreign oil has been added. Any variation from the readings of

[1] Weekly Bulletin of the State Board of Health of Massachusetts, Jan. 14, 1905.

the table exceeding 1.3 is sufficient for submitting the sample to further examination as being suspicious.

TABLE IV.—REFRACTION OF COD-LIVER OIL.

Temp. °C.	Butyro-refractometer reading.	n_D.	Temp. °C.	Butyro-refractometer reading.	n_D.
35.0	71.4	1.4732	25.0	77.5	1.4769
34.5	71.8	1.4734	24.5	77.8	1.4771
34.0	72.1	1.4736	24.0	78.1	1.4773
33.5	72.4	1.4738	23.5	78.4	1.4774
33.0	72.7	1.4740	23.0	78.7	1.4776
32.5	73.0	1.4742	22.5	79.1	1.4778
32.0	73.2	1.4743	22.0	79.4	1.4780
31.5	73.5	1.4745	21.5	79.7	1.4781
31.0	73.8	1.4747	21.0	80.0	1.4783
30.5	74.1	1.4749	20.5	80.3	1.4785
30.0	74.4	1.4751	20.0	80.6	1.4787
29.5	74.7	1.4753	19.5	81.0	1.4789
29.0	75.0	1.4754	19.0	81.3	1.4791
28.5	75.3	1.4756	18.5	81.6	1.4792
28.0	75.6	1.4758	18.0	81.9	1.4794
27.5	75.9	1.4760	17.5	82.2	1.4796
27.0	76.2	1.4762	17.0	82.5	1.4798
26.5	76.5	1.4763	16.5	82.9	1.4800
26.0	76.8	1.4765	16.0	83.2	1.4802
25.5	77.2	1.4767	15.5	83.5	1.4803
25.0	77.5	1.4769	15.0	83.8	1.4805

III. NEAT'S FOOT OIL.

Neat's foot oil is obtained by boiling the hoofs of neat cattle in water, but it is usually the custom in rendering establishments to use the whole leg below the knee, and no doubt the majority of the neat's foot oil of commerce is made in this manner.

Four samples of pure oil, the analyses of which are recorded in Table V, were obtained from the New England Rendering Co., Brighton, Mass. They were of a pale yellow color, and when cooled to 10° for the specific gravity determination remained liquid and perfectly clear. The one adulterated sample recorded in Table V became solid when cooled for the determination of the specific gravity.

TABLE V.—CONSTANTS OF PURE AND ADULTERATED SAMPLES OF NEAT'S FOOT OIL.

	Sp. gr. at 15°.	Butyro-refractometer reading at 20.	Iodine number (Hanus).
Pure oil	0.9133	63.3	71.3
Pure oil	0.9148	63.5	73.1
Pure oil	0.9145	63.6	73.0
Pure oil	0.9143	63.6	71.7
Adulterated oil	0.9167	61.5	60.0

The refraction Table VI was calculated from readings of the pure oils recorded in Table V.

TABLE VI.—REFRACTION OF NEAT'S FOOT OIL.

Temp. °C.	Butyro-refractometer reading.	n_D	Temp. °C.	Butyro-refractometer reading.	n_D
35.0	55.0	1.4626	25.0	60.7	1.4664
34.5	55.3	1.4628	24.5	60.9	1.4665
34.0	55.6	1.4630	24.0	61.2	1.4667
33.5	55.9	1.4632	23.5	61.5	1.4669
33.0	56.2	1.4634	23.0	61.8	1.4671
32.5	56.5	1.4636	22.5	62.1	1.4673
32.0	56.7	1.4637	22.0	62.4	1.4675
31.5	57.0	1.4639	21.5	62.7	1.4677
31.0	57.3	1.4641	21.0	62.9	1.4679
30.5	57.6	1.4643	20.5	63.2	1.4680
30.0	57.9	1.4645	20.0	63.5	1.4682
29.5	58.2	1.4647	19.5	63.8	1.4684
29.0	58.4	1.4649	19.0	64.2	1.4686
28.5	58.6	1.4650	18.5	64.5	1.4688
28.0	58.9	1.4652	18.0	64.8	1.4690
27.5	59.2	1.4654	17.5	65.1	1.4692
27.0	59.5	1.4656	17.0	65.4	1.4694
26.5	59.8	1.4658	16.5	65.6	1.4695
26.0	60.1	1.4660	16.0	65.9	1.4697
25.5	60.4	1.4662	15.5	66.2	1.4699
25.0	60.7	1.4664	15.0	66.5	1.4701

The readings of castor and cod-liver oils agree with those published by Lewkowitsch, Henriques, Utz, and Liverseege.

IV. ESSENTIAL OILS.

The essential oils used in this work, the results of which are reported in Table VII, were obtained from reliable manufacturers and dealers as pure oils for the understood purpose of establishing constants, and every indication is that the oils were pure.

TABLE VII.—CONSTANTS OF A FEW ESSENTIAL OILS.

Oil.	Sp. gr. at 15°.	Polarization 100 mm Ventzke.	n_D 20°.	25°.	30°.	35°.	40°.
Peppermint	0.9056	— 79.7	1.4614	1.4593	1.4573	1.4553	1.4533
Sweet orange	0.8501	272.8	1.4731	1.4708	1.4685	1.4662	1.4637
Bitter orange	0.8523	266.6	1.4738	1.4715	1.4691	1.4667	1.4643
Lemon[1]	0.8590	175.0	1.4744	1.4722	1.4700	1.4677	1.4655
Citronella	0.8996	— 31.6	1.4813	1.4790	1.4768	1.4745	1.4722
Nutmeg	0.9090	45.7	1.4834	1.4841	1.4787	1.4764	1.4740
Lemon grass	0.9070	— 10.0	1.4858	1.4836	1.4814	1.4792	1.4770
Spearmint	0.9310	—126.4	1.4858	1.4836	1.4814	1.4792	1.4770
Cloves	1.0502	— 3.1	1.5313	1.5290	1.5268	1.5245	1.5222
Wintergreen[2]	1.1865	— 0.1	1.5363	1.5340	1.5318	1.5295	1.5272
Cassia	1.0666	0.7	1.5998	1.5973	1.5949	1.5925	1.5901
Cinnamon	1.0395	— 0.3	1.6029	1.6009	1.5988	1.5968	1.5948

A large number of essential oils have been examined during the course of drug inspection of this department, and the following list gives the maximum variation of the refraction from readings in Table VII of those oils found by other tests to have been pure.

TABLE VIII.

Wintergreen oil	±0.0018
Peppermint oil	±0.0017
Cassia oil	±0.0013
Clove oil	±0.0012
Lemon oil	±0.0011

A sufficient number of the other oils of known purity have not as yet been examined to state the variations in refraction, but at least two reliable samples of each oil obtained from different sources have been tested for refraction with closely agreeing results.

THE DETECTION OF METHYL ALCOHOL.[3]

BY HEYWARD SCUDDER.

Received April 24, 1905.

THE TESTS for the detection of methyl alcohol are used chiefly to distinguish it from ethyl alcohol, so their value is dependent first on a sharp distinction from ethyl alcohol, then on their delicacy and rapidity. In the following description the standard of delicacy

[1] Readings are all averages from a large number of samples.

[2] Made from the sweet birch.

[3] Presented before the New York Section of the American Chemical Society in February, 1905.

will be taken as the quantity of ethyl alcohol that can be detected in ethyl alcohol. Most of the tests will show very much smaller quantities of methyl alcohol in water, but their use for such a purpose is practically unknown.

ODOR TESTS.

This is made by adding to the solution, salicylic acid and concentrated sulphuric acid and warming, thus forming methyl salicylate which is supposed to have a characteristic odor (of oil of wintergreen). In experiments made on eight persons I found that none of them could distinguish between ethyl and methyl alcohol by this test, because the odor of ethyl salicylate so strongly resembles that of methyl salicylate. If told that both alcohols were present a difference in odor was often noticed, but if solutions of unknown content were given, *e. g.*, two tubes of methyl or two of ethyl alcohol, the test failed even when comparative tests with the alcohols were made.

All tests dependent on odor are unsatisfactory because it is impossible to make accurate comparative tests. After smelling any odoriferous body, probably on account of persistence of the odor in the nasal passages, or possibly from slow reactivity of the olfactory nerves, it is not possible for an ordinary person to have an accurate perception of the odor of a second body. This can readily be shown experimentally, most surprising mistakes being made after the sense of smell is once blunted. In making color tests the comparison is direct and the subjective effect of memory is eliminated.

I have been told that this test has been used in trials, for adulteration of liquors, to show juries the difference between the two alcohols, the point being made that there is a difference in the rapidity of the production of the odor as well as in the quality. I consider the test unreliable and not sufficiently rapid to be an improvement on the test by oxidation with a hot copper spiral and testing for the oxidation product by resorcin. The difference in color between the condensation products of acetaldehyde and resorcin and formaldehyde and resorcin is great enough to be appreciated by any juror.

COLOR TESTS.

In the Riche and Bardy[1] test the methyl alcohol is converted

[1] *Compt. Rend.*, **80**, 1076 (1875).

into methyl aniline which is then tested for. The test is too long and slow to be of much use to-day.

In all the other tests the alcohol is oxidized to formaldehyde, methylal or formic acid. The color test is then applied to this oxidation product. Methylal gives the same reaction as formaldehyde in almost all tests. If ethyl alcohol is present, either the color test must be given only by the oxidation product of methyl alcohol—as in oxidation to the acid, formic acid giving a dark color with silver nitrate while acetic acid gives no color—or enough of the corresponding oxidation product of ethyl alcohol must be removed to prevent interference with the color. The difficulty of fulfilling these conditions is the chief cause of failure in the tests used. It is practically impossible to control oxidation so as to get a good yield of formic acid and the tests for its detection are not very delicate. The removal of all the acetaldehyde without some loss of formaldehyde is impossible, but this method is perfectly practicable since the tests for formaldehyde are extremely delicate. The fact that pure ethyl alcohol, when oxidized by any of the methods used in the tests for methyl alcohol, gives some formaldehyde is not sufficiently considered. It has been shown[1] that when ethyl alcohol is oxidized by a heated copper spiral, formaldehyde is formed in small amounts. I have found that this is also true when ethyl alcohol is oxidized in cold dilute solution by potassium bichromate and sulphuric acid, or by potassium permanganate and sulphuric acid, enough formaldehyde being made to give the gallic acid test.

Therefore, it is obvious that the test used to show the presence of formaldehyde, after oxidation of the alcohol, must not be too delicate or it will apparently show the presence of methyl alcohol when none is really there. This is the defect of the gallic acid reaction[2], an extremely characteristic test for formaldehyde and one little obscured by the presence of other compounds, but so delicate that it is given by solutions of ethyl alcohol, cane-sugar and a great variety of compounds after oxidation by a heated copper spiral[3].

The tests that follow are grouped by the reagent used for the

[1] Mulliken, Scudder: *Am. Chem. J.*, **24**, 446 (1900).

[2] The solution to be tested is mixed with 0.2 cc. of a saturated alcoholic solution of gallic acid and poured on top of (not mixed with) concentrated sulphuric acid in a test-tube. A contact ring of blue or green and blue shows the presence of formaldehyde.

[3] Mulliken, Brown and French: *Am. Chem. J.*, **25**, 115 (1904).

production of the color, in order to make more clear a general understanding of the difficulties and of the sources of error.

REAGENT, SILVER NITRATE.

Miller Test.[1]—This consists in oxidation in the cold by potassium bichromate and sulphuric acid, distillation and testing the distillate for formic acid by silver nitrate. Allyl alcohol and acetone are said to give the same reaction. It is noted that a trace of formic acid or some other reducing agent is formed from ethyl alcohol. The test is not delicate and is of little importance.

REAGENT, LEAD PEROXIDE.

Trillat Test.[2]—This consists in oxidation in cold dilute solution by potassium bichromate and sulphuric acid, under which conditions methyl alcohol is said to give methylal, ethyl alcohol to give acetaldehyde, acetal and acetic acid. The acetaldehyde is removed by distilling 25 cc. The next 100 cc. distilled contain the methylal. One-half of this is digested in a closed flask with dimethylaniline at 70-80° for three hours, forming tetramethyldiaminodiphenylmethane. The solution is made alkaline and the excess of the dimethylaniline distilled. The residue is acidified by acetic acid and a little lead peroxide added. On boiling, a blue color appears, if methyl alcohol is present. It is said to show 0.2 per cent. methyl alcohol in ethyl. The time required for the test is about five hours.

The difficulties are numerous. If all the acetaldehyde is not removed by the fractional distillation, what remains may give a color that resembles or interferes with that from methylal. Since some methylal distils over with the acetaldehyde it is not safe to distil off much more than 25 cc. to remove the latter, for if only a small amount of methyl alcohol is present, the loss might be sufficient to spoil the test. The dimethylaniline and the lead peroxide must be very pure or the color may be affected. In distilling off the excess of dimethylaniline (this procedure is necessary because dimethylaniline gives a violet or blue color with lead peroxide) some methylal is lost as may be shown by tests. I have found it easy to be sure of the removal of all the dimethylaniline, by filtering through a wet filter before distilling. No special care is necessary in

[1] Allen's "Commercial Organic Analysis," Vol. I, p. 81 (3d Ed.).

[2] *Ann. Chim. Anal. Appl.*, **4**, 42 (1899); *Compt. Rend.*, **128**, 438 (1899); *Bull. Soc. Chim.* (3) **21**, 445 (1899).

acidifying after the removal of the dimethylaniline, since a great excess of acetic acid has no effect on the color. The amount of lead peroxide used is actually a variable quantity. The directions call for four to five drops of a suspension in water. In addition to the variable strength of different samples, another error is possible here, since the amount of lead peroxide present will depend on how thoroughly the suspension is shaken before use. If too little is used, the color is faint. If too much is used, the color changes from blue to brown, though the effect of heat in deepening the color still persists.

The depth of color is supposed to be proportional to the amount of methyl alcohol originally present, but it is sometimes difficult to get this result. I have found a much fainter color from a solution that contained 10 per cent. of methyl alcohol than from one that contained 1 per cent., though the procedure was the same in each case.

I believe that the development or deepening of the color by boiling is characteristic. Acetaldehyde, after digestion with dimethylaniline and subsequent treatment as in the Trillat test, gives in the cold a color varying from green-yellow to green-blue. Dimethylaniline in the cold gives with lead peroxide a color varying from green-yellow to pure blue, but in both cases the color does not deepen on boiling, while the blue from methyl alcohol develops only on boiling. The color may be diminished or changed by the use of the wrong amount of lead peroxide, but here again boiling makes a characteristic deepening, if methyl alcohol was in the original solution tested, so that if there is a color in the cold that disappears or is not deepened by boiling, no methyl alcohol is present (provided the test has gone well). If the color deepens on boiling, even if it is not a pure blue but possibly a green-blue or brown, methyl alcohol is present.

Wolf[1] states that pure ethyl alcohol gives the same reaction as methyl when the Trillat test is used, but that if the digestion with dimethylaniline is made at room temperature for twenty-four hours instead of at 70-80° for three hours the test works perfectly. He claims that 0.1 per cent. of methyl alcohol can be shown in ethyl alcohol in this way. Since he makes no statement of the effect of heat on the color, the value of the improvement is doubtful, for it is possible that the color obtained from ethyl

[1] *Ann. Chim. Anal. Appl.*, **4**, 183 (1899).

alcohol was due to the incomplete removal of acetaldehyde.

Robine[1] gives an elaborate criticism of the Trillat test, and suggests several small changes in the procedure. His most essential points are the recommendation to make a blank test of every fresh sample of dimethylaniline; the necessity for having pure lead peroxide and for using the proper amount; the difficulty of removing all the acetaldehyde without loss of methylal and the fact that the test is spoiled unless all the acetaldehyde is removed. The presence of acetaldehyde is sometimes indicated by a yellow color of the solution and a precipitate of aldehyde resin after the excess of dimethylaniline has been distilled off. His criterion for the presence of methyl alcohol is that the final test must give a pure blue appearing hot, disappearing cold. Any shade of blue that has green in it, green-yellow or pure green is not to be regarded, since it may come from incomplete removal of acetaldehyde.

Since Robine notes the effect of heat on the color, it would appear probable that he tried heating in the cases where the color was due to acetaldehyde, but the fact that in such cases no deepening occurs when the solution is boiled is not mentioned by him. This differs from my observations previously given.

It is evident that the Trillat test must be used with care. It is delicate and fairly rapid, but the test may be spoiled not only by slight variations in the procedure, but also by causes of unknown origin which occur when the procedure is strictly followed. It is certainly not a test to be recommended to persons of limited knowledge of chemistry.

REAGENT, RESORCIN.

Mulliken-Scudder[2] *Test.*—In its simplest form this consists in oxidizing a dilute solution of the alcohol by plunging into it several times a spiral of copper wire heated to redness. The formaldehyde formed is tested for by adding one drop of a 0.5 per cent. aqueous solution of resorcin and pouring, without mixing, on top of a little concentrated sulphuric acid in a test-tube. A contact ring and, on very gentle shaking, flocks of a characteristic red color appear, if formaldehyde is present. Acetaldehyde gives a ring and flocks of a color that varies from yellow to brown. This

[1] *Ann. Chim. Anal Appl.*, **6**, 128, 171 (1901); Cf. Euler, *Ber.*, **37**, 3411 (1904), and Bach, *Ibid.*, **37**, 3986 (1904), on the unreliability of the Trillat test for formaldehyde, which is the same as the methyl alcohol test beginning with the digestion with dimethylaniline.

[2] Mulliken, Scudder: *Am. Chem. J.*, **21**, 266 (1899).

shows 8-10 per cent. of methyl alcohol in ethyl. The time required is about five minutes.

The modified form[1] is more delicate. The oxidation is carried out in the same way, but the acetaldehyde is removed by boiling the solution down about one-half. This may be done over a free flame for rapid work. In boiling down, some formaldehyde is always lost, and the more rapid the boiling the greater the loss. Therefore, it is advisable to boil down at 25-30° under diminished pressure in order to get the best results. Where little formaldehyde is present the formation of flocks is slow, so in this modified form after the solution is brought in contact with the sulphuric acid it must be allowed to stand for three minutes, then shaken very gently for a minute, causing the two liquid surfaces in contact to mix, but not allowing rapid or excessive mixing. If only a very little formaldehyde is present, rapid mixing prevents the formation of flocks, although it has little or no bad effect when much formaldehyde is present. The formation of flocks is a necessary part of the test, a contact ring of the proper color not being considered sufficient evidence, since acetone and dimethylethylcarbinol both give red contact rings. Methyl esters and ethers, methylal and secondary and tertiary butyl alcohols give the same reaction as methyl alcohol in this test. This would indicate that whenever a methyl group and oxygen are close together and not bound firmly to the remainder of a compound, oxidation may produce formaldehyde, the amount formed probably being dependent on the relative attraction between the different groups in the compound. This test shows 2 to 3 per cent. methyl alcohol in ethyl. The time required is about twenty minutes. One great advantage of the test is that the formation of flocks of characteristic color gives a very positive indication, much more so than the production of a contact ring or of a temporary color.

United States Pharmacopoeia Test.—Sadtler[2] states that the committee for the revision of the Pharmacopeia found resorcin more delicate than phloroglucin as a test for the formaldehyde produced in the oxidation of methyl alcohol. They give the following directions. Ten cc. of the solution to be tested, having a concentration of about 10 per cent. (in testing liquors or alcohol, the proper dilution must be made), are placed in a test-tube

[1] Mulliken, Scudder : *Ibid.*, **24**, 444 (1900).
[2] *Am. J. Pharm.*, **77**, 106 (1905).

surrounded by cold water. It is oxidized by plunging a red hot spiral of copper wire—of specified dimensions—to the bottom of the test-tube and holding it there one to two seconds. This is repeated five to six times. The filtered solution is boiled gently till any odor of acetaldehyde ceases to be clearly distinguishable. To the cooled solution one drop of a 1:200 aqueous solution of resorcin is added and the mixture is floated on top of concentrated sulphuric acid in a test-tube. After standing three minutes the tube is gently rotated. If no rose-red ring appears, less than 2 per cent. of methyl alcohol is present. The time required for the test is about fifteen minutes.[1]

Mulliken Test[2].—The alcohol is oxidized by a heated copper spiral, ammonia is then added and the solution is boiled gently in a dish till the odor of ammonia has disappeared. The acetaldehyde is thus driven off and the formaldehyde is converted into hexamethylentetramine. Concentrated hydrochloric acid is then added and the solution brought momentarily to boiling to decompose the hexamethylentetramine. The formaldehyde set free is tested for by resorcin as in the Mulliken-Scudder test. The test shows 10 per cent. methyl alcohol in ethyl, and an expert is said to be able to detect less than this amount.

This test is no more delicate than the simple form of the Mulliken-Scudder test so that its advantage is not apparent. Theoretically, the method is one that promises well. Ammonia unites with formaldehyde very rapidly to form hexamethylentetramine, a compound that is stable on boiling and does not distil off to any extent, while acetaldehyde-ammonia is decomposed by heat and the acetaldehyde can be completely driven off by boiling. There are two defects in the process that I have not been able to overcome in any way. The addition of ammonia retains all the formaldehyde produced in the oxidation of ethyl alcohol, so that any delicate test applied after the decomposition of the hexamethylentetramine, whether the test is for the formaldehyde or for the ammonia, is given both by ethyl and methyl alcohol.

[1] When I read this paper, I gave the outlines of a rapid test that would show 2 per cent. methyl alcohol in ethyl. Since that time Sadtler has published the test just given. The procedure of my test differed in several points, but the two are so much alike that it seems inadvisable to burden the literature with the details of mine. The fact that with such differences in procedure the results obtained are the same, shows that the pharmacopoeia test can be recommended to persons of limited chemical experience.

[2] Provisional Methods for Analysis of Foods (U. S. Dept. Agriculture, Bureau Chemistry, Bull. 65, 73 (1902).

The oxidation by a copper spiral does not produce enough formaldehyde from methyl alcohol to allow as a test the use of the formation of some compound of hexamethylentetramine, such as the tetraiodide or the mercuric chloride compound, although both these compounds (which give difficultly soluble precipitates) can be used to detect the presence of quite small quantities of hexamethylentetramine. No precipitate is formed from quantities of hexamethylentetramine sufficient to give, after decomposition, fairly thick flocks in the resorcin test. In this decomposition some formaldehyde is always lost, since other compounds besides ammonia and formaldehyde are formed. It is advisable to boil for fifteen or twenty seconds or longer to get the maximum amount of formaldehyde.

REAGENT, FUCHSINE.

Another use of hexamethylentetramine gave promise but fails at times for reasons that I cannot discover. The solution is oxidized by a heated copper spiral, filtered, an excess of ammonia added and then boiled down about two-thirds. It is then cooled and 2 cc. of fuchsine aldehyde reagent added. The sulphurous acid in this decomposes the hexamethylentetramine and the aldehyde set free instantly colors the solution. A blank of pure water and fuchsine reagent is made, and the difference in color and the time noted. In this way it was possible to show 1 per cent. methyl alcohol in ethyl in fifteen minutes. But at times pure ethyl alcohol would give a color as deep and as rapidly formed as that from methyl alcohol. As a rule ethyl alcohol when oxidized gives a color that is very faint at first and does not deepen for so long a time that the distinction between it and that from methyl alcohol is sufficiently marked to make a good test.

REAGENT, PHLOROGLUCIN.

Acetaldehyde in amounts less than 0.01 per cent. gives no reaction with an alkaline solution of phloroglucin in the Haigh and the Prescott tests, but will give a reaction with 1.0 cc. or 2.5 cc. of alkaline phloroglucin as used in the Sanglé-Ferriére test. In large quantities—over 0.1 per cent.—it will also give a color with the phloroglucin solution in the Haigh test. Formaldehyde in very small amounts gives a color permanent for several minutes. The color is said to be pure red. Actually it depends on the relative concentrations of the formaldehyde and the phloroglucin, varying

from yellowish red through pure red to violet-red. Since, in any solution to be tested, the quantity of methyl alcohol present may be anywhere from 1 per cent. to 100 per cent., oxidation will produce a very variable amount of formaldehyde, but the conditions of any test call for a fixed amount of phloroglucin; so the color may be pure red or may be any of the shades mentioned.

Sufficient formaldehyde is formed in the oxidation of ethyl alcohol to give a color with phloroglucin, though this color is fainter than that obtained from the oxidation of solutions containing over 10 per cent. of methyl alcohol. The color is said to differ in quality from that obtained from oxidized methyl alcohol. I have not found this statement to be true, for the reason just given.

The color obtained from oxidized methyl alcohol is said to be much more permanent than that given by oxidized ethyl alcohol. While this is true, the color given by ethyl alcohol often lasts for a number of minutes, so that it is impossible to distinguish between ethyl and methyl alcohol either by this criterion or by the difference in color, without making a comparative test with ethyl alcohol. In some experiments on the duration of the color (the oxidant was a heated copper spiral), a 10 per cent. aqueous solution of methyl alcohol gave a red that lasted for ten minutes without any noticeable fading; then it gradually grew lighter. At the end of twenty minutes the color was still well marked. At the end of one hour there was no color. A 20 per cent. aqueous solution of ethyl alcohol gave a distinct red that lasted for six minutes, then began to fade. At the end of fifteen minutes the color was very faint. A 20 per cent. aqueous solution of a mixture of 2 parts methyl alcohol and 98 parts ethyl alcohol, boiled down one-half after oxidation, gave a red that was deep for one minute, then faded but was noticeable for more than ten minutes. A 20 per cent. solution of ethyl alcohol similarly treated gave a color that faded from the beginning and was hardly noticeable after three minutes.

The full depth of color is sometimes not reached for one to two minutes. The duration of the color is lessened by stirring.

When the solution is boiled, the color changes to a clear brown-yellow. This same color develops on boiling solutions that have become colorless. When cooled, after boiling, the color from methyl alcohol is permanent for one to two minutes, then fades

more or less slowly, while the color from ethyl alcohol becomes very faint or disappears as soon as the solution is cold. This disappearance or fading of color in the case of ethyl alcohol is noticed with certainty only when an excess of alkali is added, since the phloroglucin solution as ordinarily prepared will give, after boiling, a faint violet in the cold. The excess of alkali destroys this violet color. When there is doubt as to the presence of methyl alcohol, on account of the faint or transient color obtained by the ordinary test with phloroglucin in the cold, the question can often be settled definitely by the addition of an excess of alkali, boiling and noting the depth and permanence of the color of the cold solution.

Whenever phloroglucin is used as the agent to detect formaldehyde in testing for methyl alcohol, a comparative test with pure ethyl alcohol must always be made, since it is impossible to state definitely the exact color or the exact duration of the color that will be obtained from varying quantities of methyl alcohol. In making this comparative test each solution must be added to the phloroglucin solution at the same time, so that the intensity and permanence of the colors may be judged by direct comparison.

Prescott Test.[1]—In this test the alcohol is oxidized by a heated copper spiral, hydrogen peroxide is added to destroy the acetaldehyde, the excess of hydrogen peroxide is removed by sodium thiosulphate and the formaldehyde tested for by phloroglucin. This shows 5 per cent. methyl alcohol in ethyl. It is difficult to get correct results with this test, because the action of the hydrogen peroxide and the thiosulphate seem to go wrong at times. The Haigh test is much more satisfactory.

Haigh Test.[2]—In this test the alcohol is oxidized by a heated copper spiral, the acetaldehyde removed by boiling the filtered solution till little or no odor is left and the phloroglucin test used to show the presence of formaldehyde. The color from methyl alcohol is said to last two to three minutes, that from ethyl alcohol to be faint and quickly to disappear. This shows 5 per cent. methyl alcohol in ethyl. The time required, including the blank of ethyl alcohol, is about fifteen minutes.

The test is as satisfactory as any that uses phloroglucin. By adding alkali and heating the solution after it has been mixed

[1] *Pharm. Archiv.*, **4**, 86 (1901).
[2] *Pharm. Review*, **21**, 404 (1903).

with the phloroglucin (as previously described) it is possible to show 3 per cent. to 4 per cent. methyl alcohol by this test. The fact noted by Haigh that after one-half hour to one hour the solution from ethyl alcohol gives a blue color, is due in my opinion to the phloroglucin alone (possibly the color comes from some oxidation reaction) and has nothing to do with ethyl alcohol or its oxidation products.

Since acetaldehyde gives no color with alkaline phloroglucin, the question naturally arises, what is the reason for its removal in the Prescott and the Haigh tests? The answer is very simple—there is no need of removal. The working of the test has been misunderstood. When ethyl alcohol is oxidized, sufficient formaldehyde is produced to give a fairly deep and permanent color with alkaline phloroglucin solution, which is quite a delicate reagent for the detection of formaldehyde. The processes employed for the removal of acetaldehyde remove at the same time so much formaldehyde that the reaction with phloroglucin is reduced to a minimum. When methyl alcohol is present, sufficient formaldehyde is left to give a well-marked reaction. The experiments on the duration of color, given under the general treatment of the phloroglucin reaction, show this very clearly.

Sanglé-Ferrière-Cumiasse Test.[1]—This consists in oxidation of a cold, dilute solution by potassium permanganate and sulphuric acid. The excess of permanganate is reduced by tannin, the solution is made faintly alkaline and the manganese dioxide filtered off. The filtrate is tested by alkaline phloroglucin. It is said to show 1 per cent. methyl alcohol in ethyl.

The test has a simple procedure, but the length of time necessary to oxidize the alcohol in order to get satisfactory results seems to vary with the room temperature, the amount of alcohol present and the method of adding the sulphuric acid. The recommendation is made to confirm the test by acidifying and testing with gallic acid. This confirmation I regard as valueless, because of the great delicacy of the gallic acid test for formaldehyde. Ethyl alcohol often gives with phloroglucin quite a deep color, not the faint color mentioned in the description of the test.

CHOICE OF TESTS.

This will vary with circumstances. Unless there is supposed

[1] *Ann. Chim. Anal. Appl.*, **8**, 82 (1903).

to be only a very small amount of methyl alcohol present, I should recommend trying first the simple Mulliken-Scudder test which shows 8 per cent. to 10 per cent and takes but a few minutes; next the Pharmacopeia test which shows 2 per cent. and takes fifteen minutes. If that gave no indication at all, the Trillat test should be used, but if there was any indication of the possible presence of methyl alcohol or a suspicion that it was there, I should advise rather than use even the Trillat test to concentrate by distillation through a Hempel tube or Le Bel-Henninger tube or some such device and then to use one of the shorter tests. This can be done much more quickly and easily than most persons suppose. In experiments to test the efficiency of the process when only small amounts of liquid are available, I used 25 cc. of a mixture of 1 per cent. methyl alcohol and 99 per cent. ethyl alcohol. This was fractionated through a Hempel tube made of glass tube 22.5 cm. long, 1.7 cc. in diameter filled with glass beads about 3 mm. in diameter. The beads held about $3\frac{1}{2}$ cc. of liquid that would not drain back into the flask. Three fractionations were made, taking the first time 15 cc., then $7\frac{1}{2}$ cc. and finally 2 cc. One cc. of this last fraction was diluted, oxidized by a heated copper spiral, boiled down one-half over a free flame and tested by resorcin. Moderately thick red flocks appeared. The total time consumed was one hour (this includes the time taken in allowing the liquid to drain back into the flask, a procedure necessary when such small quantities of liquid are being fractionated in this way). The Trillat test would have taken five hours. The Sanglé-Ferriére-Cumiasse test is claimed to have a delicacy sufficient to show this amount of methyl alcohol, but I am doubtful about its indications. None of the other tests is sufficiently delicate to use in such a case.

The great value of the resorcin test is in the positive evidence given and the advantage of having some idea in a rough way of the quantity of formaldehyde present. The formation of flocks of characteristic color shows positively the presence of a certain amount of formaldehyde and no comparative test with ethyl alcohol is necessary. If there is only a contact ring and no flocks, there is very little formaldehyde present. When more is present there will be scanty, small flocks. When much is present, the flocks are thick and abundant.

MIXTURES.

In consequence of the great number of organic compounds, it is impossible to devise a test that will show a particular compound in any possible mixture. Certain general principles can be given, and by the aid of these and by a clear understanding of what the test used will show and what are its possibilities of error, the detection of methyl alcohol ought to be certain except when it is present in very small quantities and there is not sufficient material to allow of concentration.

If formaldehyde is present, it must be removed, if any of the oxidation tests are used, since they are all dependent on conversion of the alcohol to formaldehyde or methylal. This may be accomplished by digestion with ammonia; by digestion cold with excess of sodium bisulphite for four to five hours[1]; by digestion at 70-80° in a stoppered bottle with resorcin and sulphuric acid for two to three hours;[2] or by boiling with a return condenser with aniline and phosphoric acid.[3] The liquid is then distilled, the formaldehyde remaining behind in combination. The distillate should always be tested for aldehyde to make sure that the removal is complete. Other means that may prove useful in certain cases are digestion hot with sodium sulphite[4] or wth hydrazine sulphate.[5] When difficulty is found in removing all the formaldehyde, it is often possible without further treatment to make a rapid test which either will show the presence of methyl alcohol or will make further investigation desirable. Under these conditions little formaldehyde will be present and the resorcin test used before oxidation will show only a contact ring. When the solution is oxidized and the resorcin test again applied, if methyl alcohol is present, the increased amount of formaldehyde will be shown either by the presence of flocks or by thickening of the ring. The presence of flocks in such a case would be almost conclusive evidence of the presence of methyl alcohol. Fractional distillation is often of great help in such cases. Gnehm and Kaufler[6] state that in the estimation of methyl alcohol in formaldehyde, when the formaldehyde is condensed with sodium sulphanilate

[1] Bamberger: *Z. angew. Chem.*, **17**, 1246 (1904).
[2] Mulliken, Scudder: *Am. Chem. J.*, **24**, 449 (1900).
[3] Allen, Chattaway: *Analyst*, **16**, 113 (1891).
[4] Lemme: *Chem. Ztg.*, **27**, 896 (1903).
[5] Pfaff: *Ibid.*, **26**, 701 (1902).
[6] *Z. angew. Chem.*, **18**, 93 (1905).

and the alcohol distilled off, the distillate always contains small quantities of compounds having the characteristic odor of formaldehyde and the power of reducing silver nitrate, but that these compounds are unsaturated bodies of unknown nature.

Other aldehydes can be removed by digestion with resorcin and sulphuric acid, or with aniline and phosphoric acid. Their presence is indicated by the usual aldehyde reactions or by the resorcin test.

Phenols and bases will combine with any formaldehyde that may be made in the course of a test. They must therefore be removed—by distillation from sodium or potassium hydroxide in the case of phenols (this treatment also removes acids)—by distillation from dilute sulphuric acid in the case of bases.

Various compounds such as coloring-matters, etc., can be removed by simple or fractional distillation, by filtration through bone-black with or without previous treatment by lime, or by extracting the alcohol with water and testing the aqueous extract after distillation.

It is best to test only solutions wholly soluble in 2 to 3 parts of water, that will distil between 50° and 100°.[1]

CHEMISTS' CLUB, New York City.

THE ESTIMATION OF FAT IN INFANT AND INVALID FOODS.

BY C. B. COCHRAN.

Received May 4, 1905.

IN THE year 1889 there was published in the *Journal of Analytical Chemistry*, page 381, a new process for determining the percentage of fat in milk, cream and skimmed milk. Since that time I have found this process capable of giving very satisfactory results in the determination of fat in condensed milks, infant foods, confections, etc., to which substances the usual methods of fat extraction with ether, or low-boiling gasoline in a Soxhlet apparatus, seem to be inapplicable.

The difficulty of extracting the fat from the dry residue of a diluted, sweetened, condensed milk by the usual fat solvents has been fully appreciated for many years, and other methods have been devised for making this determination.

[1] Mulliken, Scudder: *Am. Chem. J.*, **24**, 447. The question is here treated entirely from the standpoint of the resorcin test, but the general principles remain the same.

At the present time probably the most widely used method of estimating fat in condensed milk is the modification of the Babcock process devised by Prof. A. E. Leach[1]. As is well known, the Babcock volumetric process fails when applied to sweetened condensed milks, on account of the charring action of strong sulphuric acid on sugar. Leach overcomes this difficulty by removing the sugar in solution while he retains the fat in the precipitated curd. By Leach's device, the Babcock process is made applicable to condensed milks because of the fact that the sugar and fat can be largely separated through the agency of the curd of the milk. In cases where the fat cannot thus be separated from sugar, or other objectionable substances, which might produce a precipitate of carbon under the influence of strong sulphuric acid, Leach's modification is of no service. In infant foods where the percentage of sugars and dextrin is high, neither Leach's method nor the usual gravimetric methods seem applicable, and it is in samples of this character that my process, although among the oldest of the rapid volumetric processes for estimation of fat in milk and cream, may still be useful.

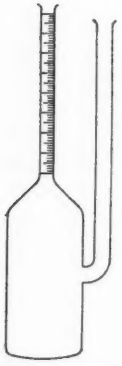
The following results of experiments made by my assistant, Mr. H. M. Loomis, show very clearly the difficulty encountered in attempting to extract the fat in infant foods by the usual method. A sample of Horlick's malted milk gave 1.91 per cent. of fat by extraction with petroleum ether for forty-eight hours in a Soxhlet apparatus, while 8.7 per cent. was obtained by the volumetric process. Borden's malted milk gave, by the method first mentioned, 0.83 per cent. fat; by the second, 6.30 per cent. Professor McGill, by extraction with petroleum ether, found 1.41 per cent. of fat in a sample of Horlick's malted milk[2].

In several samples of infant foods, the residue from forty-eight hours' extraction with petroleum ether, was subjected to the volumetric process, and an additional quantity of fat was obtained. To more carefully test the accuracy of the process, a mixture of powdered casein, sugar, dextrin, and fat of known proportions was made in the laboratory and submitted to analysis. Unfortunately the results of this experiment are not to be found, but I can state that the results obtained by the test were in close accord with the amount of fat actually used in preparing the mixture.

[1] This Journal, **22**, 589.

[2] See "Food Inspection and Analysis," by A. E. Leach, p. 271.

The following is a description of the process as applied to milk:



5 cc. of the milk to be tested are delivered through the side tube into a flask of the construction shown in the figure. To this is added 2.5 cc. of 80 per cent. acetic acid, and an equal volume of concentrated sulphuric acid. After mixing the milk and acids, the flask is set in hot water until the contents turn a coffee color. It is then removed and cooled; 4 cc. of ether are added, and mixed thoroughly with the liquid. The flask is again placed in hot water and the ether allowed to boil off. A layer of supernatant fat will then be found floating on the surface of the liquid. By pouring hot water down the side tube, the melted fat is raised into the narrow graduated tube at the top of the flask where its volume can be read. The flask is graduated for 5 cc. of milk to read in tenths of per cent.

In case of infant foods, introduce through the side tube 1.72 grams of the powder, then add 5 cc. of water and bring the powder as far as possible into solution. Now proceed in the same manner as with milk. Multiply the result by 3 (1.72 grams is one-third of the weight of 5 cc. of milk).

To determine fat in sweetened condensed milk, to 1 part by weight of the milk, add 4 parts, by weight of water and mix thoroughly. Proceed with this sample the same as with milk. Multiply result by five.

The style of flask used is a matter of no importance provided there is sufficient means of escape for the ether vapor and a sufficiently delicate means of reading the fat column. In case the larger tube is made to enter at the top of the flask, it should reach only a short distance into the bowl so that it will allow free escape of the ether vapor through it. In the flasks used by me, the bowls have about the same volume as the bowls of the Babcock milk flasks.

The process above described will, I believe, give reliable results in cases where a process, like the Babcock, requiring the use of large quantities of sulphuric acid would fail. The charring action of the mixture of strong acetic and sulphuric acids is less than that of the sulphuric acid alone. Furthermore, in this process, the dissolving as well as the charring action of the mixed acids de-

pends largely upon the application of heat which is under control and can be stopped at any desired point. As a matter of fact, the success of the process will depend largely on the judgment used in regulating the first heating. I have found it better to avoid charring even though solution is not obtained. At this stage a clear liquid must not be expected. After the emulsified fat has been dissolved in the ether and finally raised by the addition of hot water the fluid in the flask will appear clear or nearly so.

WEST CHESTER, PA.

NOTE.

Changes of Color Caused by the Action of Certain Rays on Glass.—While working on this subject two articles have appeared which render a detailed account of my experiments unnecessary.

Sir William Crookes[1] has noticed that glass from South America containing manganese becomes violet on exposure to the sun's rays and Franz Fisher[2] has observed the same phenomena with ultraviolet rays from a mercury vapor lamp. There are a few suggestions quoted from the papers of Sir William that I may note:

"It would be interesting to hear if travellers in other tropical countries have observed any such change of color of glass."

My samples came from New Mexico and were intensely colored.

"It is hardly conceivable that there can be a special radioactivity of the soil in certain parts of Chili and Bolivia sufficiently powerful to produce the effect."

The sand from New Mexico was not radioactive. A bottle partly buried showed the greatest change of color where most exposed to the sun's rays. Different samples that have been exposed to the sun's ray, presumably for several years, show a depth of color approximately proportional to the manganese present.

"Sunlight and radium both produce similar effects in these respects. Their modes of action are known to be, in the main, very different, but it has been clearly shown that, in general, variation in time being disregarded, what radium is capable of doing in the way of inducing chemical change, ionizing gases, producing phosphorescence, and impressing a photographic plate, sunlight will also effect."

[1] *Chem. News*, Feb. 17, 1905, p. 73.
[2] *Ber. chem. Ges.*, S. 946, 1905.

All specimens of glass that I have been able to procure contain manganese. Presumably manganese-free glass will not be made permanently violet by radium rays. S. AVERY.

NEW BOOKS.

THE AMERICAN YEAR-BOOK OF MEDICINE AND SURGERY FOR 1905. Volume I, GENERAL MEDICINE. Philadelphia, New York and London: W. B. Saunders & Co. 1905. 8vo. 701 pp. Cloth, $3.00 per volume; half morocco, $3.75.

The interest of chemists in this excellent compilation, which has been briefly reviewed through several years past, will center largely in the chapters on physiological chemistry and physiology, but in the sections on general medicine, legal medicine, pathology and public hygiene there is also much that is important from the chemical standpoint. As in former years the work is under the editorial charge of Dr. George M. Gould. The staff of writers is essentially the same as before.

While the yearbook is prepared to furnish brief reviews for medical men it will prove of almost equal value to chemists and others who may wish to keep familiar, in a general way, with the most important advances in the related science, which, in some of its specialties, is becoming each year more and more dependent on pure chemistry. J. H. LONG.

A TEXT-BOOK OF MEDICAL CHEMISTRY AND TOXICOLOGY. By JAMES W. HOLLAND, M.D. Philadelphia: W. B. Saunders & Co. 8vo. 592 pp. Cloth, $3.00 net.

In this good-sized volume, the preparation of which is evidence of commendable industry on the part of the author, an attempt is made to condense about everything that the medical student is supposed to require in chemistry, general, physical, inorganic, organic physiological, analytical and clinical. While much that is presented is very satisfactory, excellent in fact, the treatment as a whole can not be commended. In common with many writers of books for medical students the author has tried to cover too many subjects and in the necessary condensation, clearness and accuracy are too frequently sacrificed. The writer of this notice has long been opposed to the use of the term "Medical Chemistry" which seems to convey the idea that there is a peculiar kind of chemistry in which medical students should be trained from the very

beginning of their courses. There can be no greater mistake. Medical students need the same kind of elementary chemistry given to other students, and this should be distinguished not so much by amount of work as by quality of work. Much of the future of *scientific* medicine must depend on chemistry and the ground work for the young physician should receive as careful attention as is given to the Freshman chemistry courses in our best collegiate institutions. In a properly balanced elementary course much must be omitted as rightfully belonging to a later period.

As an example, consider the author's discussion of the Phase Rule, on pps. 42 and 43. Why this is included at all in a book for beginners it would be difficult to explain; the treatment in the present case is of such a character that the Freshman who could get anything tangible from it would be a phenomenon. Attention should be called also to several misleading definitions under the head of Polarimetry, and to the wrong use of the term "solvent," near the top of p. 124 where some other word is probably intended.

Entirely too much space is given to the subject of toxicology, which has long been the characteristic feature in the chemistry courses in some of our medical schools. The medical student has little concern with the chemical side of toxicology, that is, with the *detection* of poisons in stomach contents or complex mixtures. This is a difficult specialty which belongs to experts only. Discussions of the *actions* of poisons belong to pharmacology rather than to chemistry.

In the portion of the book devoted to organic chemistry there are very good descriptions of many compounds important in medicine. This matter appears to have been carefully selected, but a more logical arrangement of it would be advantageous.

The last 80 pages of text are given to physiological and clinical chemistry, of which urine analysis takes up the larger part. The sections on physiological chemistry proper are greatly condensed and not at all in proportion with other sections of the book. References to many of the more recent discussions in this field seem to be entirely lacking. J. H. LONG.

LABORATORY STUDIES FOR BREWING STUDENTS. By ADRIAN J. BROWN, M.Sc. University of Birmingham. New York and London: Longmans, Green & Co. 1904. 193 pp. 36 illustrations. Price, $2.50.

The author is to be congratulated upon his efforts to facilitate

the studies of those brewing students who wish to gain a thorough knowledge of the scientific principles of brewing and malting. The manual presents in a very concise and plain manner those facts which are of most important value to the practical and up-to-date brewer.

The author strives by means of practical laboratory experiments to introduce the student to the botanical as well as chemical properties of barley, hops and yeast. He describes the main requirements in their valuation and the changes which they undergo in the manufacture of beer. The book is divided into four sections.

The *first section* deals with the botanical description and technical valuation of barley, its anatomy and physiology as well as the physiological and chemical changes which take place during malting. The chapter ends with the technical as well as chemical examination of malt.

Section 2 comprises a thorough study regarding the hydrolysis of starch, the properties of the different carbohydrates and finally some experiments bearing upon the mashing process and its products in practice. This chapter closes with the methods for the analysis of beer and for the valuation of brewing sugars.

The *third section* is devoted to the physiological and chemical principles of fermentation, the study of the various organisms and their general biology. Directions are given for the preparation of pure cultures and for general bacteriological methods. The chapter concludes with some directions for the biological control in practice.

In *Section* 4 the author describes directions for the examination of hops and their technical classification and valuation.

The book also contains six tables for ready reference in the analytical methods. The book is provided with 36 illustrations which assist the student materially in the perusal of this new and welcome laboratory manual on brewing. EMIL SCHLICHTING.

THE DETECTION OF POISONS AND STRONG DRUGS, Including the Quantitative Estimation of Medicinal Principles in Certain Crude Materials. By DR. WILLIAM AUTENRIETH, University of Freiburg. Translated from the Third Enlarged German Edition by WILLIAM H. WARREN, A.M., Ph.D. (Harvard). Illustrated. 12mo. Philadelphia: P. Blakiston's Son & Co. 1905. 12 + 222 pp. Cloth, $1.50 net.

The author states in his preface that the book is intended as a concise laboratory guide for students in medicine and pharmacy and the contents of the five chapters and the appendix show that his aim has been kept well in mind.

The translator has followed the original text, giving even the references to the German instead of the U. S. Pharmacopoeia, the latter being at hand, he thinks, for the American student.

The examination for poisons is given in a systematic method. While the method is applicable to specimens furnished students it can also serve for the examination of viscera, as in a toxicological analysis.

The introduction gives directions especially with regard to the division of the viscera into several portions, each portion to be used for a group of poisons, with retention of one part as reserve material. While this will do for laboratory work it is inadvisable for forensic cases, since the quantity of poison present may be so small that a division of material might lead to negative, or doubtful results. It is wiser to operate with larger masses of the organs and to follow the alternate method the author indicates, of subjecting the residue of one operation to the processes of the next succeeding group. Thus after extracting the alkaloids the residue may well serve for the detection of metallic poisons.

The poisons are divided into four groups, the volatile, phosphorus, hydrocyanic acid, etc.; the alkaloids; the metallic poisons; and the poisons not found in the other groups, the mineral, and organic acids and the alkalies.

In the examination for the alkaloids the Stas-Otto method for their separation from each other is given, to be applied to the alcoholic extract of the specimen, which has been acidulated with tartaric acid.

Directions are given for the evaporation of the alcoholic extract on a water-bath. This is permissible for laboratory testing but should not be followed in a forensic case. There evaporation at a lower temperature should be resorted to.

More stress should be laid, too, in cases where poisoning is suspected, on a thorough purification of the several extracts as obtained from evaporating the ether, chloroform or amyl alcohol solutions, before applying any tests, and further that in such procedure the application of preliminary tests leads as a rule only to the waste of valuable material.

The author wisely insists on the destruction of organic matter as a first step in the detection of the metallic poisons. He does not lay sufficient stress however on a most thorough washing of the precipitate, obtained by the action of sulphuretted hydrogen, to

free it of chlorides, before subjecting it to the solvent action of ammonium hydroxide and sulphide.

Since copper is as a rule found in viscera, its separation at this point of the analysis, from arsenic and antimony, is important. Indeed the rule now so commonly followed in mineral analysis, of double precipitation, must be adhered to in the separation of the metallic poisons. Not until so separated should special tests be applied. It is rather remarkable that the book gives no directions for the quantitative determination of the metals, though a chapter is devoted to that of the alkaloids. In practice it is requisite to report the quantity of the metal present in each organ, if that is possible, and the quantitative estimation should precede the application of special tests, which should prove the identity of the poison beyond a doubt. The author lays stress on the latter point, quite rightly, and especially in regard to the alkaloids that they may be differentiated from the ptomaines. A single test should not be relied on, but the cumulative evidence of many tests, with no negative test to mar the record.

In view of the very extensive literature on the Marsh test, especially brought out by the labors of the British Commission, it is surprising that the form of apparatus described and illustrated should be recommended, and too, that no mention is made of the electrolytic method. It is also surprising that a "spot test" should be applied, or that the odor of the arsine should be relied on.

The Fresenius and Von Babo apparatus is faulty in that as each bubble of carbon dioxide comes up through the sulphuric acid in the drying bottle it will cause a puff in the ignition tube, liable to carry away the arsenic that should deposit on the cold portion of the glass.

The sections on blood and the bacteriological methods in testing for blood or for arsenic are important additions to the book.

Since the quantitative tests for the alkaloids follow official methods, their introduction serves a special function in the teaching of students in pharmacy.

The book is pleasing. Directions are plain, and the systematic character of an analysis is well developed.

The student is instructed not only as to the preparation of special reagents, but is given a correct description of their application to the object tested.

The book is in clear type, well divided into sections, and the illustrations are attractive. C. A. DOREMUS.